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COMPLETE CATALYTIC LABORATORIES

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Volume 1

Part 1

PROCESS AND EQUIPMENT FOR THE PRODUCTION OF FURAN FROM FURFURAL BY A VAPOUR-PHASE HETEROGENEOUS CATALYTIC METHOD

by

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Working diagrams prepared by

the staff of the Department for Technical Development,

Factory for Laboratory Equipment

Budapest

P R E F A C E

Among the new trends of the Hungarian team of Chemical engineering the investigations into the economy of operations and processes in the chemical industry play a role of increasing significance. One of the results of this study is the approval of the axioma: that, caeteris paribus, the higher is the output of a chemical plant, i.e. the larger is the amount of material flowing through the cross section of the equipment in unit time, the better is its economy. In chemical technology, this finding resulted in an increased application of catalytic methods raising the rates of reaction, and in the extensive use of continuous processes.

In the course of this development the accelerating role of the specific reaction surface both in catalysed and non-catalysed reactions has been ever more and more understood and a number of Hungarian scientists have dealt since some years with this factor of increasing the output.

The author of this book and designer of the laboratory equipment to be described here, dr. Lajos MÉSZÁROS, is one of the Hungarian chemical engineers who have made thorough investigations into the main factors of accelerating the reactions. He discussed in several papers the role of large specific surfaces in improving the efficiency of catalysts. Thus, his attention was directed to catalysis by lead-melt bed and to mercury-vapour catalysts. In his experiments he achieved conditions near to molecular dispersion, and through these he attained specific contact and catalyst surfaces larger by several orders of magnitude than those that could be obtained with conventional methods.

The author has extended his work also to some of the bordering fields and investigated the regulation of reaction temperatures, the problem of scaling up, of diffusion and the pyrophorous character of finely dispersed metal catalysts. The experiments have resulted in designing and testing a number of ingenious reactor types and in evolving the principles of scaling up. In this way he succeeded in creating a laboratory catalytic reactor lending itself excellently to conducting preliminary tests and to collect basic data for scaling up.

The author's work represents a highly significant contribution to the development of chemical engineering in this particular field: the creation of a laboratory equipment on quite novel lines for conducting continuous catalytic reactions and for the systematic recording of the parameters. This is important also from a didactical aspect, offering the students the opportunity to become familiar with this technique and to prepare plant work on a model scale. The most important feature of this equipment is that, though in a small scale, it operates continuously under the conditions as an industrial plant does, being controlled and regulated similarly to industrial apparatus.

The first equipment has been intended mainly for the decarboxylation of furfural to furan. The discussions on the following pages lay down the theoretical basis for this process, as regards reaction mechanism, catalysis, diffusion and pyrophorous effects in the reactions. The volume is terminated by detailed instructions for the operation of the equipment - going as far as to give an example for a record on the experiment - and is completed by a thorough Operator's Manual covering all the necessary details. The latter will be supplied together with the equipment by the Factory for Laboratory Equipment, the manufacturer of the apparatus.

The present work is rightly considered as one of the most significant achievements of Hungarian researches into chemical technology.

Budapest, Mai 15, 1963.

Mór KORACH

Director of the Institute for Technical Chemistry of the Hungarian Academy of Sciences

PREFACE OF THE AUTHOR

Reactors of various design for heterogeneous catalysis have been gaining ground in modern large-scale chemical industry at an exceptionally rapid pace. Every country aiming at the development and modernization of its chemical industry looks with expectation at these production methods, as catalytic plants are suited for the production, under favourable economic conditions, of large quantities of primary materials and intermediate products for processing plants. In the field of organic chemistry reactors are used particularly for the production of primary materials /thus, in petroleum processing, oxidation of hydrocarbons, production of halogenated devivatives, etc./ but they are of great importance also in almost every other field, since hydrogenation, dehydrogenation, hydration, dehydration, hydrolysis, hidroformylation, oxidation etc. and also other types of reactions are made possible by the use of catalysts. The widespread application of contact catalytic methods renders a high-degree of automation possible, effectively contributing hereby to a substantial reduction of prices in chemical industry.

The exceptional practical importance of contact catalytic methods necessitates the furthering of their propagation and consequently the organization fundamental theoretical and practical training. An adequate equipment is needed for this purpose in research and educational institutions.

The METRIMPEX Hungarian Trading Company for Instruments, Budapest, undertakes to supply both research and educational institutes with a suitable equipment offering a complete set of laboratories for the realization of vapour-phase heterogeneous catalytic methods, manufactured by the Factory for Laboratory Equipment.

The set of laboratories will prove particularly useful:

1. in experiments for the production of primary materials in research institutes for organic primary materials, for plastics and for petroleum and natural gas;
2. besides the investigation of processes, for the development and improvement of those already in use in industry;
3. in researches into catalysts and their life-time;
4. for technical universities and postgraduate training institutes for engineers, as test and demonstration equipment facilitating the study of catalytic processes.

The complex laboratory consists of several units, and the acquisition of already one of them makes possible an extensive study of heterogenous catalytic methods and their application. The complete laboratory lends itself to realise, on a laboratory scale, a large number of industrial production methods in the field of organic chemistry. Experiments may be performed on a laboratory scale, however, they can readily be scaled up for industrial production. Prior to designing a plant for the production of some chemical compound, optimum conditions for the reaction can be determined on a laboratory scale.

The equipment has proved useful both for the development of new processes and for the improvement of existing ones, as well as for the investigation of the life-time of catalysts. The complete laboratory equipment renders the conduction of extensive research programmes possible.

The first unit of the complex catalytic laboratory is an equipment for the production of furan from furfural. The enclosed descriptions of processes make possible the determination of the optimum parameters of the reactions and their application in the design on industrial scale. Obviously,

this equipment may be used also for the investigation of any other reactions of similar type. Thus, besides others, the following reactions have been carried out with this equipment /Fig. 1./ and descriptions of these processes have been prepared.

1. conversion of furfural to furan on pyrophorous lead catalyst;

2. production of pyrrole from furan and pyrolidine from tetrahydrofuran;

3. production of maleic anhydride and fumaric acid from furan and furfural;

4. cracking of /ricinoileic methylricionleate methylic esther/;

5. dehydration of alcohols not sensitive to heat.

Figure 1. Syntheses starting from furfural..

The complete catalytic laboratory is planned to comprise about 20 units to permit the carrying out of chemical reactions of various types in the field of vapour-phase catalysis. The volume of the catalyst varies from 20 millilitres to 60 litres for the individual reactors. Reactors of greatly varying types, some of them designed along quite novel principles: pipe stills, pipe stills with trays, melt-bed reactors, mercury vapour reactors, disk reactors, spherical reactors, etc. have been developed, and pyrophorous metals, metal fogs, metal smokes etc., used as catalysts.

The major part of the equipment is automated which ensures the conditions necessary for the convenient and accurate observation of the experimental parameters.

The present textbook and instructions for operation are the first volume of the series, describing the physical and chem-

ical properties of furan and its derivatives and their uses in industry. In addition to other methods for the preparation of furan, it gives a detailed description of the process of oxidative decarboxylation of furfural, developed at the József A. University Szeged. This has been reported by the author at several international congresses of chemistry, and a number of patents have been granted. The book gives a survey of the contact catalytic reactors designed according to these new principles, discusses the pertinent theoretical considerations and the possibility of their use in the production of furan. Detailed description of these reactors will be given in the next volumes.

The first volume discusses the fundamental concepts of catalysis in chemistry. The role of interfacial phenomena in catalytic reactions is pointed out, with special respect to the conversion of furfural into furan. The laws governing the adsorption of gases and the test methods of adsorbents are discussed in detail. The preparation of pyrophorous metals and their possible application in catalysis are described.

The various apparatuses and instruments are precisely described and instructions are given for their operation. The book deals exhaustivly with the preparation and testing of catalysts. The experimental apparatus for the production of furan is treated in detail and complete technological instructions are given for the production of furan. Directives for the study of specific factors characteristic of the reactions and for the evaluation of the individual parameters of influence are provided. The book includes also necessary information on the maintenance and repair of the equipment.

Additional volumes on the operation of machines of further laboratory units will be compiled on the same principles, as

supplement to the respective equipment. We intend hereby to supply new, modern, useful means for the mastery of fundamental research work in contact catalysis, thus contibuting to the economic realisation of novel up-to-date organic chemical processes.

Szeged, Mai 10 1963

dr. Lajos MÉSZÁROS

Part 1

THEORETICAL SURVEY AND LITERATURE

Chemical Properties of Furan and Derivatives. Their Application in Industry. Conversion of Furfural to Furan by a Vapour-Phase Catalytic Method.

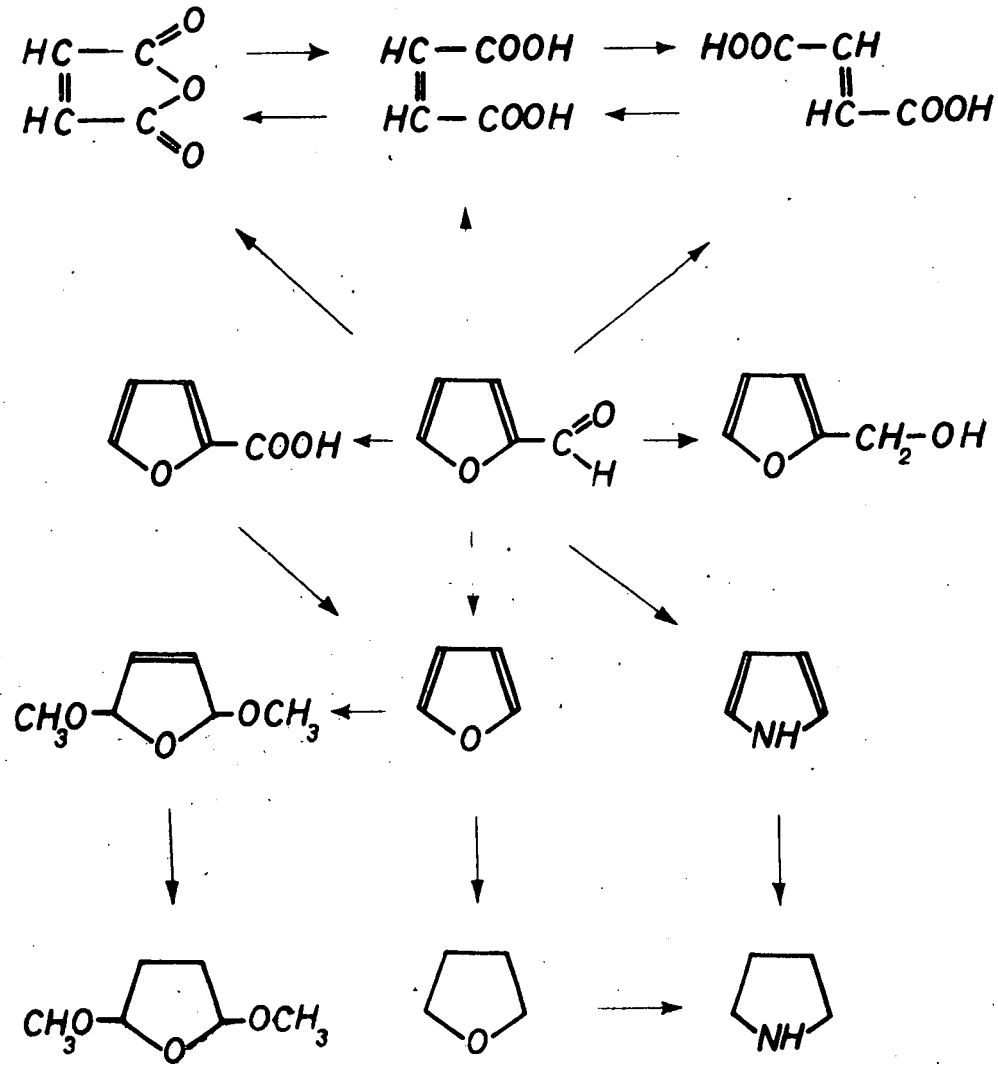


Figure 1

Some of the reactions of furan chemistry that can be carried out with our equipment.

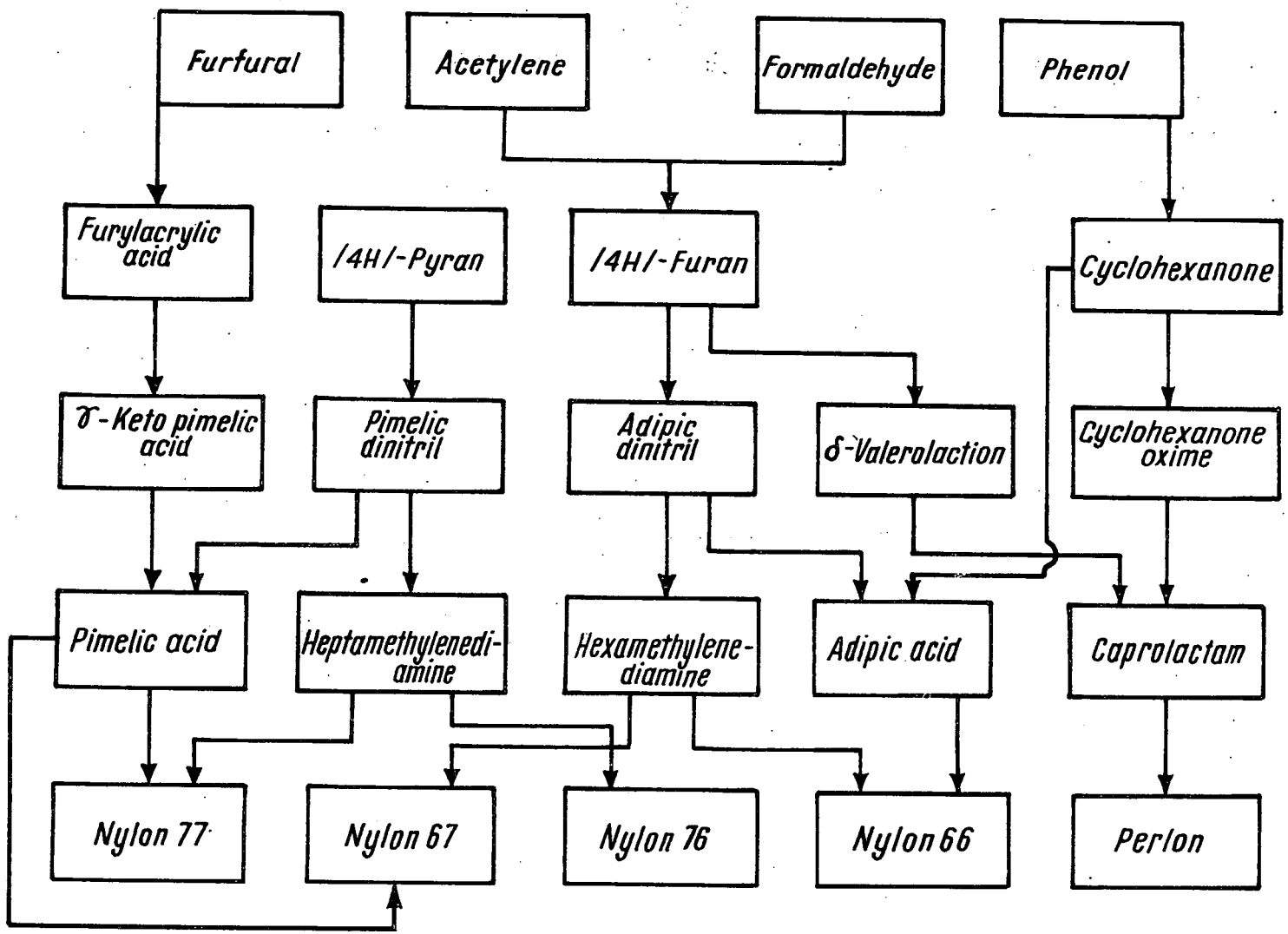
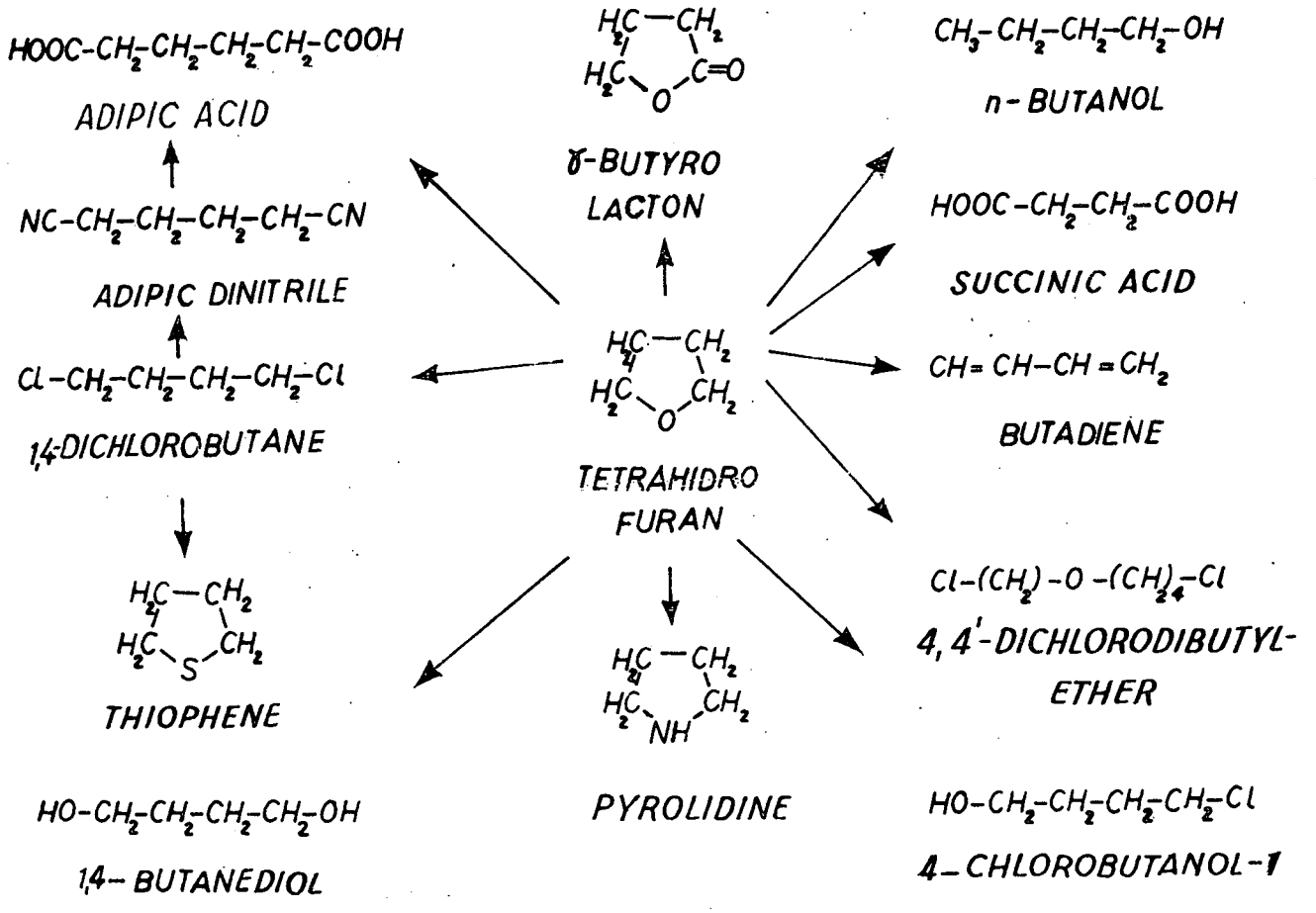


Figure 2

Starting materials for some polyamide-type plastics



3

Figure 3
Syntheses starting from tetrahydrofuran

A/ STRUCTURE AND PRINCIPAL REACTIONS OF FURAN

THE USES OF FURAN DERIVATIVES

1. Introduction

Though furfural, the parent compound of furan derivatives, was discovered as early as 1832 by Döbereiner /1/, furan derivatives became significant in large-scale industry only a century later. Furan chemistry has developed particularly rapidly during and after World War II. Furan compounds serve as themes in 4 - 5000 publications and about 3200 patents up to 1948 /237/, and the number of patents and publications has certainly doubled since that date.

Owing to the industrial and scientific interest, quite a number of books /3-5, 16, 24, 154, 158-160/ and surveys /2. 6-15, 168, 236/ dealing with this group of compounds have been published. Furan chemistry is particularly advanced in the United States of America, Soviet Union and Japan, forming one of the principal branches of large-scale organic chemical industry. The primary material used in industry is furfural, obtained in large-scale industrially under favourable economic conditions from agricultural wastes: such as corn stalk, corn cob, straw, rice shell, sawdust, shavings and other pentosan-containing cheap vegetable materials /16/.

A considerable part of the furfural produced is used in its original form in the petroleum industry as a selective solvent /195/, or due to its fungicidal property, in wood impregnation and as seed disinfectant, and it is also used as solvent for dyes and lacquers etc. The substantial part of the produced furfural is used after conversion. The most important furfural derivatives are furan, tetrahydrofuran,

tetrahydrofurfuryl alcohol, dihydropyran, furan- 2-alkyl, 2,5 dialkyl, and 2,5-dihydrofuran, 2-alkoxy and 2,5-dialkoxy derivatives, all of them serving as primary materials for the synthetis of a wide range of organic compounds /Figures 1., 2., 3./.

Besides the availability of the cheap raw materials, the huge development of furan chemistry can be explained by this wide variety of possible conversions. It is by no means indifferent that the majority of the processes can be carried out on a large-scale with fair yields by catalytic methods. Catalytic processes, the majority of them in vapour phase, have rendered a high-degree of automation possible and resulted in a further reduction of prices.

In addition to their utilization as primary materials and intermediates for the chemical industry, furan derivatives are widely used as starting materials for plastics manufactured by condensation and polymerisation, as vulcanisation accelerators in the processing of caoutchouc/zinc-dithiofuranate = Furac II., lead-dithiofuranate = Furac III/, and as a plasticizer in the plastic industry /furfural- phenyl-hydrazone/. Furfurylalcohol is a useful additive to gasolene for the removal of soot from the engine. Many furan derivatives are used as drugs. Nitro-furan derivatives /17-19/ have gained particularly wide application. A bactericide nitro- furol-semicarbazone is marketed under the name Furacin /23/. Some of them have anti-tumor properties /20-21/, others have a bacteriostatic effect on tuberculosis /22/.

The survey of literature presented here inducludes the description of the structure of furan and its important chemical reactions with special respect to their significance in industry. A short account on the preparation of furan is given. The conversion of furfural into furan is discussed in detail. The operation of the continuous vapour-phase reactors of novel principle, developed by the author and coworkers at the

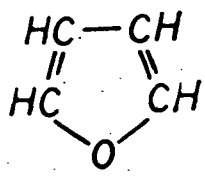
JÓZSEF A. University Szeged, and their application for the conversion of furfural to furan are described.

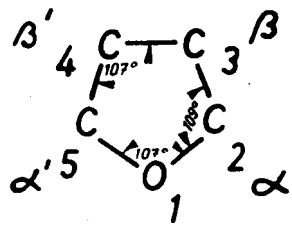
Obviously we could not present a complete survey of literature, or a full discussion of the reactors. The reactors, however, will be described in full detail in the Operator's Manuals to be supplied with the equipment.

2. Structure of Furan

The chemical character of the furan molecule is determined by interaction of the nucleophilic oxygen atom with the conjugated double-bond system. Its reactions may be interpreted by the polyfunctional character of the furan ring. In furan derivatives the effect of both ring and the side chain asserts itself. Furan possesses the characteristics of ethers, of dienes and of aromatic compounds. The dominance of one of these characteristics depends on the particular substituents, on the reaction partners and on the conditions of the reaction.

Considering furan as an aromatic system, we find that the stability of the furan ring is lower than that of benezene. Also, owing to its polyfunctional character, its reactivity is higher.





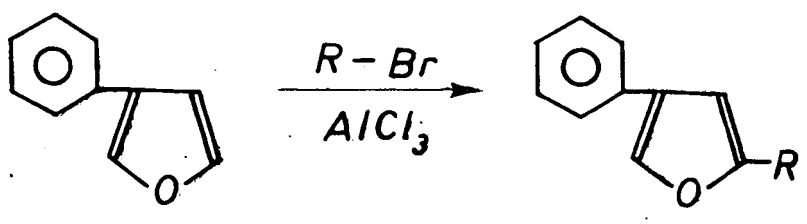
In the furan molecule the double bonds between the C_2 - C_3 and C_4 - C_5, atoms as well as the simple bond between C_3 and C_4 are purely formal ones. Schomaker and Paulig /25/ have demonstrated that the distance of the bond O-C is 1.40 Å, that of C_2 - C_3 1.35 Å, and that of C_3 - C_4 1.46 Å. Consequently, the bond C_2 - C_3 in the furan molecule has only up to 84 - 86 per cent a double bond character and the formally simple bond C_3-C_4 is approaching the nature of double bonds in 16 per cent.

Recent investigations of Moris and Pilar /26/, involving the calculation of the π electron system of furan with the L.C.A.O.M.O. method starting from the thermochemical bond energy of the C-O bond /91 cal./ have given similar results. The mentioned authors have found the following bond orders and bond distances O - C_1 : 1.089, 1,42 Å; C_2 - C_3 : 1,890, 1.35 Å ; C_3 - C_4 : 1.453, 1,45 Å. The resonance energy of the molecule has been found to range below 25 Cal./mole. Electron charge density and electron localization energy have also been computed. The investigations have shown that in the electron system of furan the O atom plays but a relatively restricted role.

Pilar /27/ has examined the C-O bond distance in furan and on the basis of thermochemical computations discussed the electron system of the furan molecule. Atom and para-localization energies have been computed /28/ on the basis of UV absorption spectra and by Hückel's M.O. method. The electron distribution found has rendered the interpretation of the chemical reactions of furan possible.

The comparison of the heat of hydrogenation of furan /-36 Cal/ with that of divinyl ether /-56,6 Cal./ indicates the aromatic character of furan which possesses by one C-C bond more and by two C-H bonds less than divinyl ether; its energy content is less by 20.6 Cal. than that of divinyl ether.

According to Gilman /29/, in the course of the Friedel-Grafts reaction, 3-phenyl-furan undergoes substitution not in the benzene, but in the furan ring. Owing to this, this author characterized furan as a "super-aromatic" compound /64,157/.



However this very reaction proves the furan ring to be polarizable.

Recently Brown and Coller /30/ have calculated the electron distributions of furan, benzofuran and dibenzofuran by the Hückel M.O. method. The Coulomb parameters of the hetero-atom and of the neighbouring C atom have shown that the electron distribution corresponds to the direction of the observed electrophilic substitution.

Le Fevre and others /31/ have determined the polarizability and polarization ellipsoide of the furan molecule. The dipole momentum of furan in CCl_4 was found to be 0.72, that of thiophene and of pyrrole 0.54 and 1.78 Debye units, respectively. The dielectric properties of furan have been investigated also by Hill /32/. Further data are available on the comparison with other five-membered aromatic systems containing one hetero-atom /33-34/.

The dielectric constants of furan in the temperature range from - 40°C to + 20°C have been determined by Lafontaine /35/.

For gaseous furan Blinc and Fahor /36/ have calculated the thermodynamical functions of industrial importance from spectroscopic data. They have established the heat capacity of furan between 300 and 1000° K and its entropy and free energy in the neighbourhood of 300° K. The heat capacity and the entropy of furan have been determined also by Bak and coworkers /37/.

Critical data of furan and other characteristics of industrial importance are to be found in the work of Kolbe and others /38/. Several physical constants of furan have recently been determined with a very high accuracy by Timmermans and Mme Hennaut-Roland /39/.

Boiling point at 760 Torr.	31,36°C
Melting point	-85,6°C
Density, $t^{\circ}/4$, at 0° C	0,96499
at 15° C	0,94485
at 20° C	0,93825
at 25° C	0,93136
Change in density per °C:	0,00145

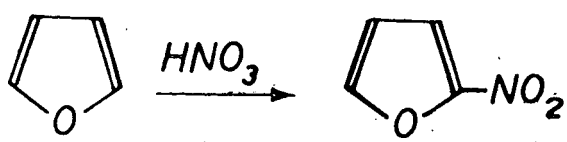
n_D^{15} : 1,42385

In recent literature, numerous investigations into the fine structure of furan and furan derivatives, carried out by physical methods, are described. Thus, NMR spectra /40/, raman spectra /41/, electron diffraction /42-43/ microwave spectra /44-45/, UV spectra /46/ and infrared spectra have been studied /47-48/. Schay and others have studied the adsorption of furan vapours on silica-gel /231/, Greene-Kelly /232/ on montmorillonite. Gas chromatography /233/ and paper chromatography /234, 235/ of furan, tetrahydrofuran and derivatives have been dealt with.

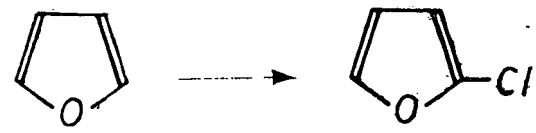
A short survey of the most important reactions of furan will be given in the following.

3. Aromatic Reactions of Furan

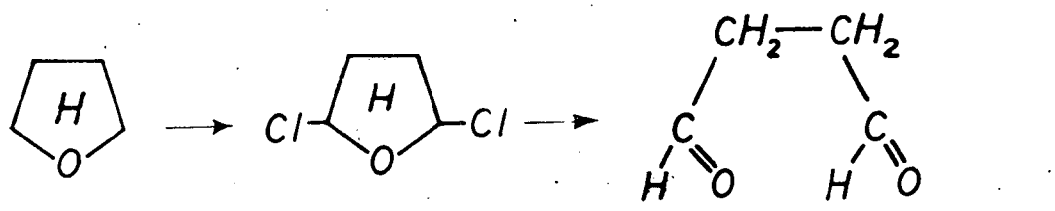
Furan can enter substitution reactions on both its α carbon atoms. With nitric acid it readily undergoes nitration to acetic anhydride /42/:



As mentioned already in the Introduction /17, 23/, various nitrofuran derivatives are of pharmacological importance and have been thoroughly examined /50-54/. According to Hillers /55/ nitrofuran derivatives are effective against Staphylococcus aureus, B. coli, Shigella flexneri etc. Furan derivatives containing nitrogen groups in side chains have also found application in pharmacology /56-57/. The halogenation by substitution of furan also occurs in positions 2- 5. /58-60/.

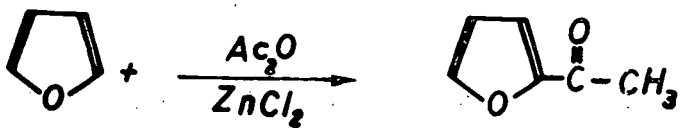


On UV-light induced catalysis at -30 to $-40^{\circ}C$ tetrahydrofuran yields 2-chlortetrahydrofuran and 2,5-dichlorotetrahydrofuran /147/. Succinic dialdehyde of great importance, can be obtained from 2,5-dichlorotetrahydrofuran in a 70 per cent yield.



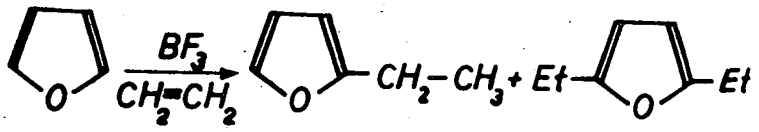
The nitro and halogen derivatives of furan are of lower stability than the corresponding benzene derivatives /61/.

With Hiller's method /62/, furan may be directly acetylated with acetic anhydride over dehydrated $ZnCl_2$ as the catalyst in a yield of 76 to 82 per cent.



2-acetyl furan may be prepared also by other ways /161/, for instance, with magnesium perchlorate as the catalyst /63/.

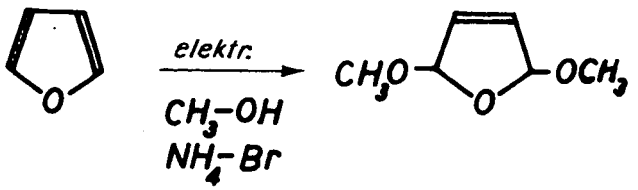
Furan may readily be alkylated by reactions of the Friedel-Crafts type /64-65/. Recently, furan derivatives are alkylated with olefines by using $FeF_2 - BF_3$ catalysts /66/. The ethylation of furan with ethylene over a BF_3 - etherate catalyst has yielded 5 - 10 per cent of 2-ethylfuran and 2 - 3 per cent of 2,5 diethylfuran /67/.



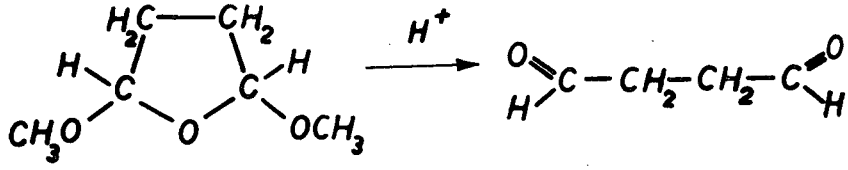
Alkylation with olefines is also possible by using a HF + + $AlCl_3$ catalyst /68-69/.

α -Alkyl furan derivatives may be obtained also by the selective reduction of alkyl - α - furylcarbinols, by hydrogenation in the presence of a special Pd + bone black catalyst /70/.

Furan and derivatives may be methoxylated by electrolysis.



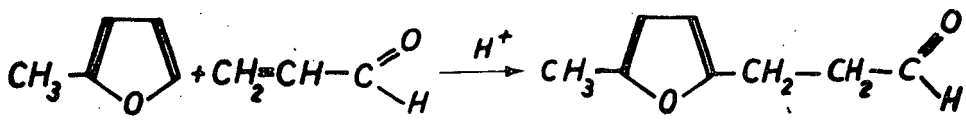
N. Clauson-Caas and others carried out fundamental work in the field of the electrolytic alkoxylation of furan derivatives /71-83/. This process is of industrial importance, as dialkoxy-dihydrofuran derivatives, on hydrogenation and subsequent acidic hydrolysis, may be converted into 1,4-dioxy compounds. Thus, 2,5 dimethoxy-dihydrofuran, on hydrogenation easily yields 2,5-dimethoxy-tetrahydrofuran, from which, by acidic hydrolysis, 1,4 dioxobutane may be obtained.



Aryloxy furan derivatives have also been prepared /84/.

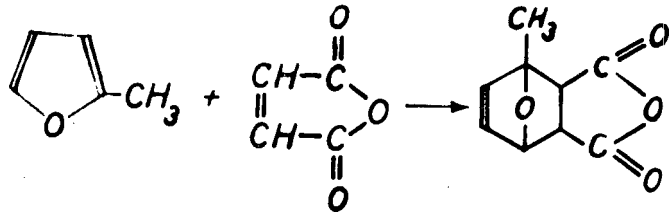
4. Use of Furan Derivatives in Diene Synthesis

Investigations into the structure of furan and theoretical considerations have shown that furan has partly aromatic characteristics. This is confirmed also by the great number of substitution reactions discussed above. On the other hand, owing to its conjugated bond system, similar to that of butadiene, furan exhibits also a tendency to diene reactions, though at a considerably lower rate than butadiene. This is supported also by the fact that between α-methyl furan and acrolein, even of the effect of catalytic acid traces, instead of a diene synthesis, rather an addition by substitution will take place /85/.

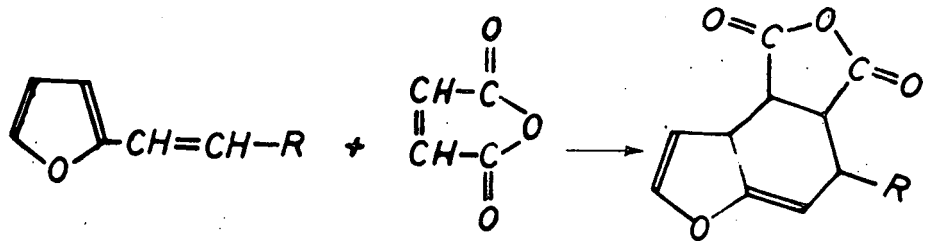


Furfural enters into reactions only as a philodiene. Similarly, under the usual conditions furan derivatives substituted in α-position with other electron attracting groups /-COOH, -CN, $-NO_2$/ /86/ or with unsaturated polar groups yield no diene adducts. If, however, in a furan derivative with an unsaturated polar side chain /as, for instance, furyl acrolein, furyl acrylic acid etc./ the unsaturated side chain is hydrogenated, it readily enters into reaction with maleic anhydride.

In the case of furan derivatives with saturated side chains, the universal reaction with the strongly philodienic maleic anhydride is the diene synthesis /87/. α-methylfurane, entering with acrolein an addition reaction, by substitution reacts with maleic anhydride as a diene.



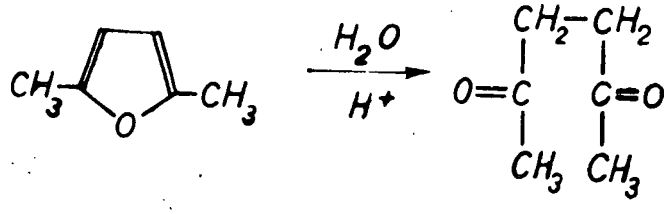
Woodward's investigations /194/ have demonstrated that also furan yields a diene adduct with maleic anhydride. It is possible to prepare tetrahydro-coumarone-dicarboxylic acid derivatives /88/ from α-vinyl-furan derivatives with maleic anhydride.



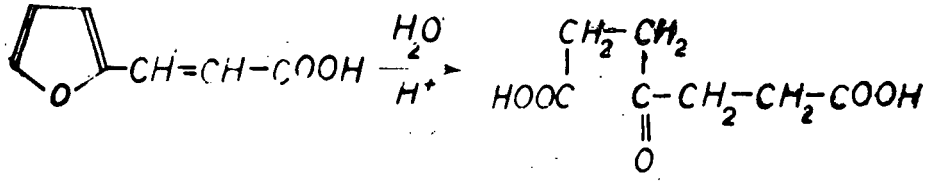
Furan derivatives are widely used for preparing oxygen-containing heterocycles by diene synthesis /89. 90/.

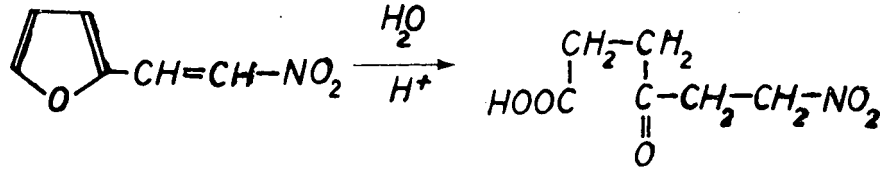
5. Reactions by the Cleavage of the Furan Ring

The etheric character of furan appears in acid catalytic reactions resulting in the cleavage the furan ring and in the formation of 1,4 dioxo compounds. Acetonyl-acetone can be produced from 2,5-dimethyl furan in an almost quantitative yield /91/.

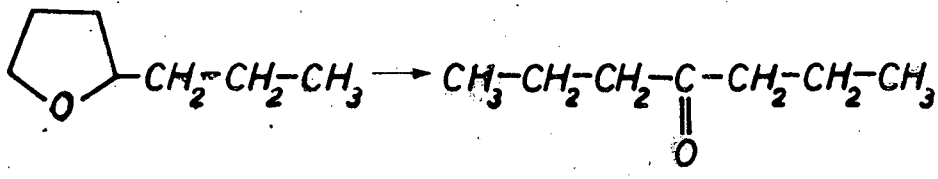


The hydrolysis of furan derivatives containing α-unsaturated substituents in position 2 results in the production of valuable oxo and substituted oxo carboxylic acids /92, 93/.

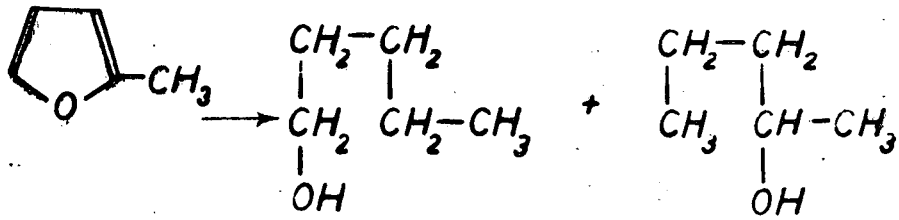




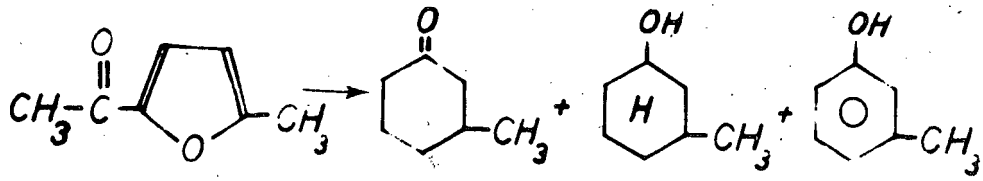
Shuikin has succeeded in carrying out the isomerization of furan derivatives into aliphatic carbonyl compounds /94/. With a Pt-bone black catalyst, at 250°C, ∝ -propyl-tetrahydrofuran has yielded 89 per cent of heptanon-4 and 11 per cent of hexane.



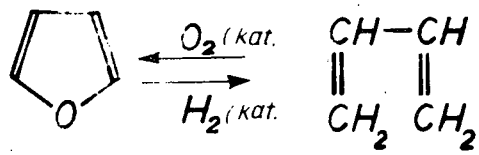
Similarly, 56 per cent nonane-4-on and 44 per cent of octane have been obtained from ∝ -amyl-tetrahydrofuran at 350° C. 2-methyl-5-ethyl furan has yielded heptane-2-on, heptane-3--on some heptanol and heptane /97/. ∝ -methyl furan gives 41 per cent of pentanol-1 and 44 per cent of pentanol-2 /95/.



Alkyl-acyl furan derivatives can be isomerized to six-membered carbocyclic compounds /96/, while 2-methyl-5-acetyl furan yields with Pt-bone black catalyst at 275°C 3-methyl - cyclo-hexanon, 3-methyl-cyclohexanol and m-cresol.

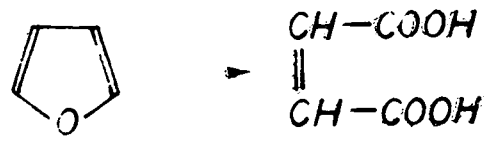


On the effect of photochemical catalysis furan derivatives undergo with ethyl diazo acetate interesting ring-expansion reactions resulting pyrone derivatives /148/. Zechmeister /149/ has found that furan similarly to other aromatic compounds /bezenene,tiophene/ decomposes on the effect of ultrasonic waves into acetylene and diacetylene. This result of theoretical interest is completed by Yuriev's work of industrial importance involving a series of investigations into the possible utilization of furan /150/.. On using active carbon containing 5 per cent of copper, this author has produced 20,1 per cent of butadiene at 425°C in a hydrogen stream.

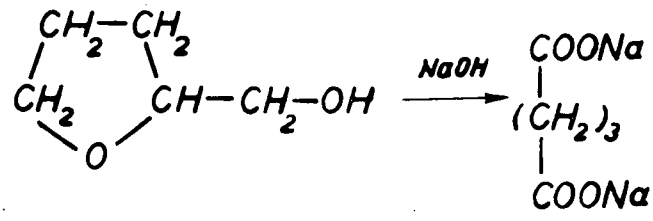


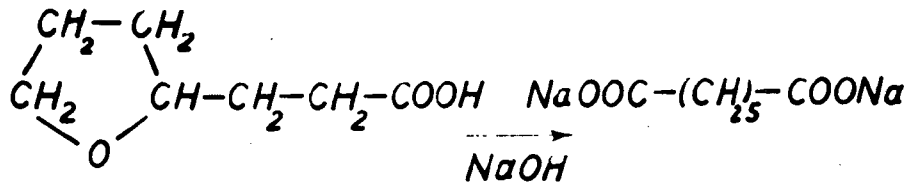
It is worth while mentioning that the reversed process, that is the preparation of furan from butadiene by using atmospheric oxygen and a manganese-molybdate catalyst has recently been carried out in a fair yield /153/.

Furan can be oxidized to maleic anhydride in a very good yield.



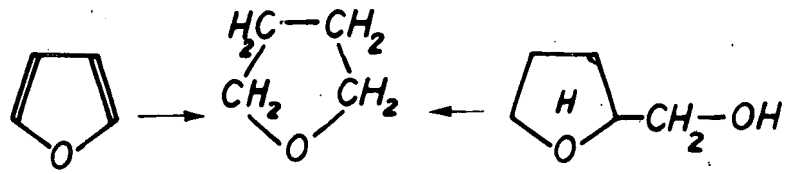
This reaction was carried ont by Hillers and Tarvida /151/ on vanadium pentoxide, molybdenum, titanium, boron and iron oxide catalysts respectively, with atmospheric oxygen, whereas we started from furfural /152/. This process will later be described in detail. Fusion of tetrahydrofuran derivatives with alkali leads to dicarboxylic acids /98/.





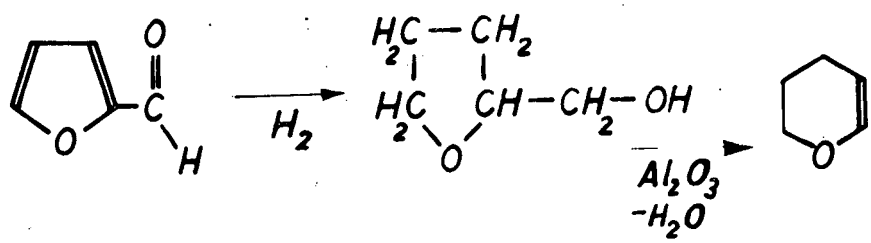
6. Hydrogenation of Furan and Derivatives

The hydrogenation of furan and furan derivatives has been thoroughly studied /236/. The catalytic reduction of furan gives tetrahydrofuran /99, 100/, one of the most important furan derivatives: Tetrahydrofuran may also be obtained from tetrahydrofurfury alcohol /101, 102/.



Tetrahydrofuran is a very important industrial solvent. It dissolves synthetic rubber, PVC, alkyde and other polymers. It is a suitable solvent for Grignard reactions. From tetrahydrofuran, a wide variety of organic primary materials can be produced on industrial scale /Fig. 3/.

Tetrahydrofuran can be polymerized and forms copolymers with ethylene, propylene oxide, dicarboxylic acids or diols /103/. Its polymers are mainly used as lubricants. By ring expansion and under splitting of water tetrafurfuryl alcohol can be converted into dihydropyran /104-105/, which, besides tetrahydrofuran, is the most important industrial intermediate, to be obtained from furfural /106/.

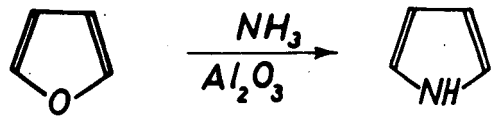


The hydrogenation of furan derivatives is often accompanied by the opening of the ring /Cf. above, 107, 108/. Hydrogenation, however, can be also carried out without hydrogenolysis /109/. Shuikin and others have throughly studied this field,

/110-114/, but other investigations /115/ of kinetic character /116/ also are known.

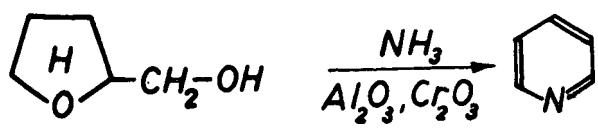
7. Synthesis of Nitrogenous Compounds from Furan Derivatives

In a tube reactor of continuous operation, pyrrole in a fair yield may be obtained from furan with ammonia and an aluminia catalyst /117, 118/.



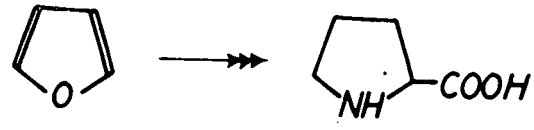
The conversion of furan derivatives into the corresponding pyrrole derivatives can be realized by an other approach /119/ also with liquid ammonia /120/.

Tetrahydrofurfuryl alcohol when treated with ammonia on a chromium oxide-aluminium oxide catalyst converts into pyridine /121, 122/.



The Klauson-Kaas method also lends itself to the synthesis of pyridine derivatives from furan derivatives/124/. Piperidine is obtained directly from furfural in a good yield /123/ and also amino derivatives can be prepared /104/.From tetrahydrofurfuryl alcohol, through halogen derivatives or dihydropirane, a number of amino alcohols and piperidine derivatives can be prepared /2/.

Recently Terent'ev and others have synthesized amino acids from furan derivatives /125-126/. For instance, in a multistep synthesis they succeeded in obtaining DL-proline through 2-acetyl furan, in a yield of 14 per cent, referred to furan /127/.

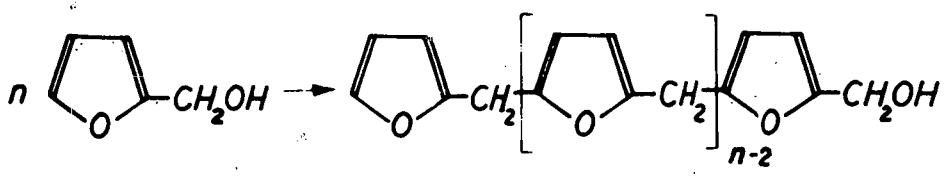


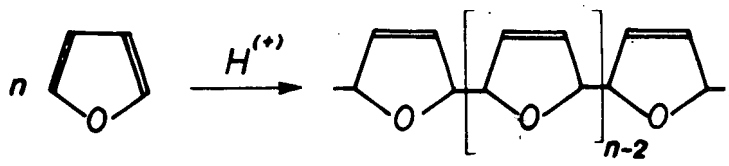
Also other pyrrolidine-carbonic acid derivatives have been prepared from furan /128/. Some furan amino derivatives, condensed with formaldehyde, are of importance in plastics industry /129/.

8. Use of Furan and its Derivatives in Plastics Industry

Besides their use as basic materials in chemical industry, furan and its derivatives find wide application also in plastics industry /168/.Literature on the use of furan derivatives in plastics industry is rather extensive and a great

number of patents have been published in this field /2,3/. Owing to the importance of the problem for large-scale industry, research work is going on and new publications appear day by day. Depending on the particular conditions, furfural itself may undergo various types of polymerization /130/, and also furfuryl alcohol /131/, furan and tetrahydrofuran can be polymerized /103/.





Synthetic resins have been prepared recently from furan in the presence of epoxides, and after-curing with Friedel-Crafts catalysts /136/.

Sultanov and Abduvaliev have thoroughly investigated the polycondensation of furan with $ZnCl_2$ as catalyst /138/. At 20°C in 12 hours a polymer of 23 000 molecular weight was obtained without the opening of the ring. The polymer is insoluble in organic solvents and does not decompose up to 400°C. Polymerization at 40 - 50°C has resulted in elastic polymers of 12 000 molecular weight, with a melting point as low as 90°C.

As shown by the latest test results /139/ furan and 2-methylfuran may be polymerized in hexane also on using an $R_3Al-TiCl_4$ catalyst. Furan yields a polymer with a melting point not lower than 320°C and 2-methylfuran not lower than 260°C.

Several other examples for the use of furan /140/ and its derivatives, for instance, of furfuryl alcohol /141/ in the polycondensation of plastic materials are found in the latest publications. The product of the disproportionation reaction of furfural /142/ as well as 2,5-furancarboxylic acid prepared from the former also find application in plastics industry /143/.

The furan-maleic acid adduct is suitable for the preparation of formed plastics /144/. The kinetics of the polymerization of 2-vinyl furan acrylic acid, prepared from 2-furan acrylic acid /145/ was the object of researches by Andreieva and Koton /146/.

Furan resins possess quite a number of outstanding properties. They are resistant to acids, alkalis and organic solvents. Reinforced with glass fibres they obtain excellent mechanical properties /137/.

Polyamide-type plastics on furan basis, obtained by condensation, are of paramount importance /132-135/. Through tetrahydrofuran, 1,4-dichlorobutane, adipic nitrile, adipic acid or hexamethylenediamine, furan can be converted into Nylon 66, and through tetrahydrofuran, δ -valerolactone and caprolactam into perlon. Some of the polyamide type plastics that may be prepared from furfural are shown in Figure 2.

Naturally, also other amide-type condensation plastics have been prepared from furan derivatives /129/.

B/ PRODUCTION OF FURFURAL. PROCESSES FOR THE PREPARATION OF FURAN FROM FURFURAL

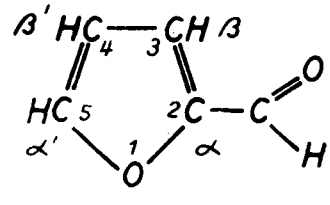
1. Introduction

The first presequisite of the use of furan derivatives in large-scale industry is the possibility of cheap furfural production. As pointed out above, this condition is completely fulfilled. In the following, the properties of furfural and the reaction mechanism of its formation will be shortly described, some of the latest methods of its production pointed out and processes of furan preparation starting from furfural discussed in detail. Constructions and working principles of the novel type reactors, developed at the József A. University, Szeged by the author and co-workers, and their application in the preparation of furan will be presented. More details on this subject will be found in the Experimental Part of this Operator's Manual and in the volumes to follow.

2. Properties and Production of Furfural

Döbereiner, in 1832, was the first in preparing furfural /1/. The structure of furfural has been established by the work /16, 166/ of a number of authors.

Its molecular structure and the numbering of atoms are as follows:



It must be noted that the β and α atoms, that is to say, - C_4 and C_5, often are denoted as γ and δ.

Freshly distilled furfural is a colourless liquid, which, on standing, turns yellow, then gradually brown and black. With

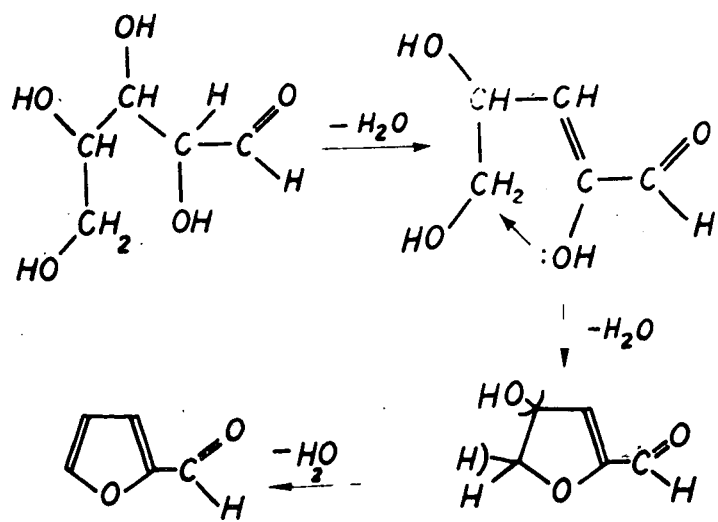
water vapour it readily volatilizes. The main physical data of the substance are the following:

Molecular weight	96 082	Melting point	-36,5°C
d_4^{20}	1,1598	n_D^{20}	1,52608
Boiling point	161,7°C		

The vapour tension of furfural, its solubility in various solvents and other characteristics of industrial importance have formed the object of extended research work /156/.

The analysis of furfural and derivatives is another field of scientific research thoroughly elaborated. Owing to the importance of the problems involved, special manuals have been published on the subject /159-160/.

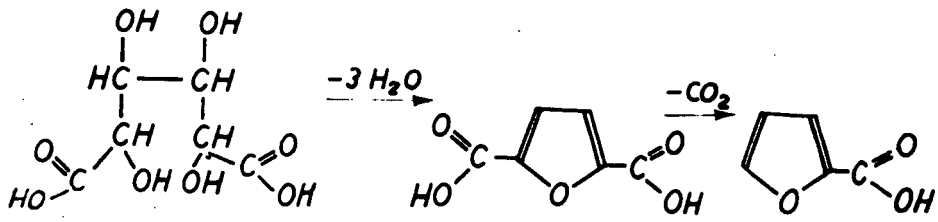
The most important sources of furfural are the pentosans found in plants. Pentosans $/C_5H_8O_4/_n$ are polysaccharides of colloidal character formed by the polymerisation of pentoses $/C_5H_{10}O_5/$. Pentosans form the hemicellulose of plants. Their degree of polymerization ranges between 120 and 200, that is to say, about a fifth of that of cellulose. As they occur in an unbound state, they are easily extracted from plants. Pentosans can be hydrolyzed to pentoses, and with the elimination of three molecules of water, furfural may be obtained. The dehydration of pentosans to furfural can be described by the following reaction scheme:



Actually, the process is not a simple dehydration, as the dehydrating agents in general use /$ZnCl_2$, F_2O_5, H_3PO_4 etc/, produce but insignificant quantities of furfural. However a dehydration resulting in the production of furfural proceeds in the presence of a certain quantity of sulphuric acid or hydrochloric acid. In spite of extensive investigations, /165, 162-163/, the mechanism of the reaction has still not been cleared up.

Schoenemann /187/ has studied the kinetics of the conversion of pentosans into furfural in aqueous acidic solutions and has determined the optimum conditions of the reaction. When the formed furfural was continuously removed, the yield increased. This author markedly contributed to the elucidation of the mechanism of the reaction.

Newth /166/ very thoroughly discussed the mechanism of the conversion of hexoses into furan derivatives. D-glucose, on loosing three molecules of water is converted into 3-oxymethylfurfural. Similarly, mucic acid, formed by the oxidation of D-galactose converts, on losing three molecules of water, into furan-2,5-dicarbonic acid, then, on elimination of carbon dioxide, into furan-2,5 carbonic acid /pyromucic acid/.



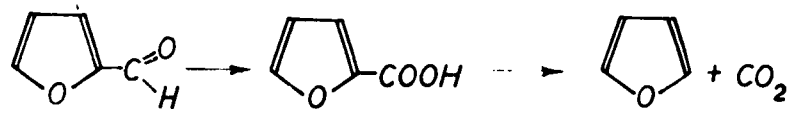
There are several hundreds of patent specifications for the production of furfural, mainly from vegetable wastes /167/. Thus, we can but mention here some of the most important processes. In the first line, we shall point out recent literature and describe a few fundamental methods.

One of the worlds largest furfural producers, Quaker Oats Co. /USA/, extracts furfural from oat husks /169-170/ with 5 per cent sulphuric acid and water vapour of 4 kg/sq. cm pressure /150° C/, in autoclaves, applying treatment periods of 6-8 hours, and attaining a yield of about 10 per cent.

In the Soviet Union a particularly great number of processes for the large-scale production of furfural have been developed /167/. One of the most interesting techniques for the production of furfural is the thermic process used in the Dniepropetrovsk works /171/. Furfural is produced by the pyrolysis of wood in the presence of 0,9 per cent sulphuric acid, at 450 to 550°C in autoclaves with treating times of 24 hours /172/. Other methods, starting from wood waste /173/, and from sunflower seed husk /174/, are also known. In recent literature, the processing of a vide variety of vegetable materials /wood, straw, corn stalk etc/ by continuous hydrolysis is dominant /175-178/. Also sulphite lyes may be used /185-186/.

3. Preparation of Furan from Furan Carboxylic Acid

On a laboratory scale, furan is produced from furfural mostly through furan carboxylic acid. At 30 - 35°C in the presence of NaOH, over a CuO catalyst containing a small percentage of Ag_2O, furfural is converted into furan - 2 - carboxylic acid in a yield of 93,7 per cent. Furan - 2 - carboxylic acid may be converted into furan by decarboxylation in quinoline over a Cu catalyst in a yield of 82,4 per cent /183/.

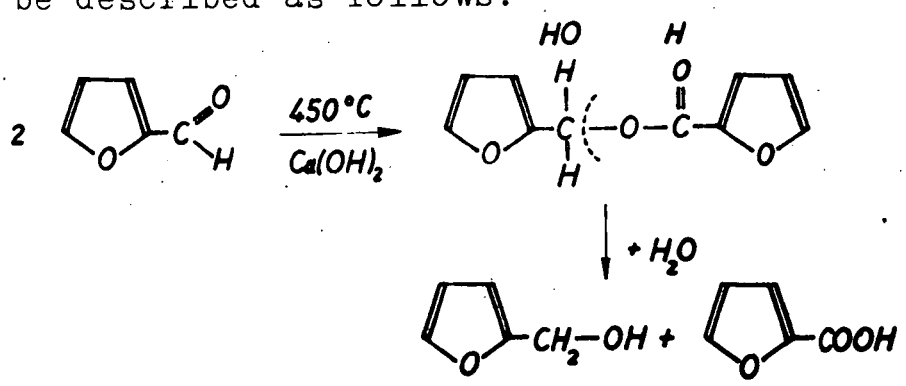


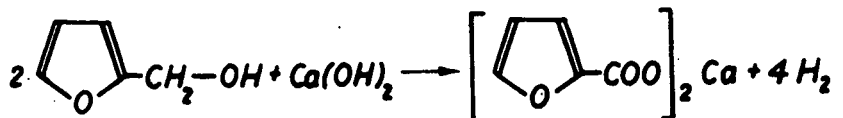
On a laboratory scale, furan - 2 - carboxylic acid can be produced also with H_2O_2 in a fairly good yield /189/. By bubbling furfural through a mixed Ag_2O catalyst suspension, 91 per cent of furan carboxylic acid is obtained /228/.Furan- - 2 - carboxylic acid can be converted into furan by thermic decarboxylation. The process has been described in several laboratory manuals and in a Japanese patent /190/.

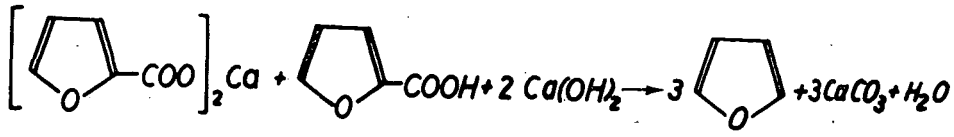
4. Preparation of Furan by Cannizzaro Reaction

The first works of industrial importance for the decarboxylation of furfural date from 1932 and the following years /191-193/.An iron tube was filled with soda lime and at 350°C furfural vapours were passed through it. Furan was produced in a 86 per cent yield, though this figure could not always be attained.

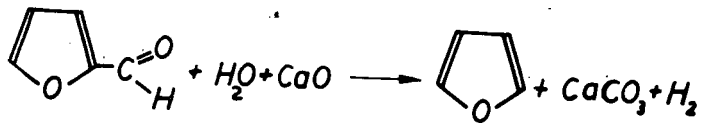
Decarboxylation with CaO has become a process that could safely be used in industry mainly as a result of Hiller's works /196/. It is based on the capability of furfural to undergo Cannizzaro reaction - a property common with other aromatic aldehydes -and its disproportionation into furfuryl-alcohol and furan carboxylic acid. Under the conditions of the reaction, also furfuryl alcohol is converted by the known Hell reaction into furan-2-carboxylic acid /197/ then furan carboxylic acid is decarboxylated.The mechanism of the reaction can be described as follows:







Summarizing the partial reactions the process may be represented by the equation:



S. Hillers throughly studied the above process. He used CaO in lumps of 5-8 mm. The temperature interval examined was 420 to 510°C the molar ratio of water and furfural varied between 5:1 and 30:1. The optimum temperature ranged between 450 and 460°C, the optimum molar ratio of furfural - water between 8:1 and 11:1, and the optimum contact time from 3 to 30 seconds. By using furfural and CaO of technical grade, Hillers obtained 70-72 per cent of furan of technical purity. To obtain one part by weight of furan 5 parts by weight of CaO were required. As the catalyst contained traces of furoyl furoate Hillers concluded that, in accordance with the mechanism outlined above, the reaction begins by a Tischenko-Cannizzaro process. Earlier, also Shur and Kozin carried out decarboxylation experiments with the use of CaO, /198/, but they could achieve only a 43,7 per cent yield even at the optimum temperature of 350°C.

Cass and Cliver's patent specification /199/ describes a process in which furfural passes through a reactor filled with CaO or $Ca/OH/_2$ catalyst at a temperature between 350 and 500°C for a contact time of 15 to 30 seconds.

Noyozi and co-workers have attained a good yield by the following method: Through a quartz tube, containing 100 parts of CaO, they passed a mixture of 25 parts of furfural and 80 parts of water vapour at 400° C. They obtained 14,2 parts of furan /213/.

For the conversion of furfural to furan, also other methods, based on the Cannizzaro reaction, are known.

Recently the hydrolysis of pentosan-containing vegetable materials, seeds /200/ or wood /201/ is carried out together with the processing of the aqueous furfural solution directly into furan. For instance, the product obtained by steam distillation is passed over a $Ca/OH/_2$ catalyst heated to 400°C, to obtain furan in a continuous process /200/. In a similar manner also the pyrolytic processes have been further developed, and furan was produced practically in a single operation from turf by pyrolysis /24/ or from wood by dry distillation /225/.

5. Catalytic Decarboxylation of Furfural

Various methods are known for the catalytic decarboxylation of furfural. Wilson's process is worth while mentioning /203/, who in a hydrogen stream and over a Ni or Co catalyst has prepared furan and some methylfuran from furfural at a temperature of 280 to 290°C /202/.

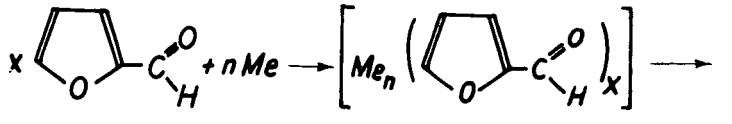
The oxides of metals of the VIIIth group of the periodical system are also suitable as catalysts for the decarboxylation of furfural /204/, at atmospherric or reduced pressure in a medium free of oxygen or in a hydrogen stream. Outstanding results have been obtained with $Fe/CO/_5$ on an aluminium carrier, at 370°C, in a nitrogen stream free of oxygen, or with Pt-black on kieselgur etc.

According to a patent of E.I.du Pont de Nemours and Co., furfural is heated in the presence of Pd catalyst /205/ to give furan. Eschinazi's process is essentially the same /223/.

Catalytic "decarboxylation" processes are mostly performed in the presence of water vapour. On the effect of metal alloys at temperatures ranging from 300 to 500°C furfural is converted into furan, CO_2 and hydrogen. In the course of the reaction, the oxygen of water oxidizes the formyl group of furfural to a carboxyl group and as the process takes place above the decarboxylation temperature, furan carboxylic acid decomposes into furan and carbon dioxide.

This process is generally denoted as decarboxylation, though in the end-gases but little carbon monoxide is found, whereas carbon dioxide and hydrogen occur in a nearly stoichiometric ratio /206/. Moreover, it is possible that CO present in traces is formed by the reduction of CO_2.

Aliev /224/ is also of the opinion that the process involved is a decarboxylation. First the metal catalyst forms a carbonyl complex with furfural, then, at high reaction temperatures, the furfural-metal complex decomposes to form, metal carbonyl and furan. On reaction with water the metal carbonyl disintegrates into metal and formic acid, then, from the latter CO_2 and H_2 are formed. According to Aliev, the mechanism of the reaction is as follows:



$$Me_n(CO)_x + X \text{ (furan)}$$

$$Me_n(CO)_x + X\,H_2O \rightarrow Me_n + X\,HCOOH$$

$$X\,HCOOH \rightarrow X\,CO_2 + X\,H_2$$

Vándor has also discussed the mechanism of the decarboxylation reaction in detail /230/. He found that the amount of

furan formed on decarboxylation in the absence of steam ranges only 30 to 40 per cent, and in the end gases mainly CO is present.

As the main reason for the poor yield is excessive resinification, in this author's opinion it is obvious that direct decarboxylation occurs and polymerization takes place when CO is eliminated. On the other hand, in the presence of steam, the yield in furan is 80 to 85 per cent, and the end gases contain CO_2 and H_2 in an equimolecular mixture. Kinetic examinations of this author have shown that in the presence of excess steam the decarboxylation of furfural takes place as a reaction of approximately second order. From this, he concluded that the reaction should be considered as a Cannizzaro type conversion taking place in the vapour phase. He is of the opinion that the direct oxidation of furfural to furan carboxylic acid and the subsequent decarboxylation are in contrast to the observed reaction of second order, as furan carboxylic acid decarboxylates very quickly, and the partial pressure of steam, as it has also been supposed in the Cannizzaro mechanism, may be considered as constant.

According to Whitman's patent specification /206/ furfural is converted into furan in a 85 to 90 per cent yield. ZnO modified with V, Cr, W, Mo or U oxides is used as catalyst in this process. Furfural vapours in a molar ratio of steam:furfural within the range from 2:1 to 6:1 are passed over the catalyst above 200°C. Karmil'ciks and Hillers /207, 214/, over an aluminium, chromium, zinc and manganese oxide mixed catalyst at 450°C and at a molar ratio of 25:1 of water: furfural attained a conversion of furfural to furan in a yield of 95 per cent. Diluted aqueous furfural solutions obtained by the hydrolysis of pentosans provide suitable also without the isolation of furfural. The activity of the catalyst, however, decreased due to the precipitation of hydrocarbons on the surface of the catalyst. Already after 10-20 hours 5 per cent of carbon was found on the surface of the catalyst.

Owing to this, the catalyst needed regeneration every 10-11 hours by blowing with air at 500 - 550°C. To absorb the furan the contact gases are bubbled through furfural, benzene, toluene or xylene at room temperature. After absorption, furan is distilled off and the solvent can be used again. In the process of Karmil'cik and coworkers, absorption proceeds at 97 - 100 per cent and the recovery of furan at 92 - 95 per cent /215-216/.

Karmil'cik and others have also developed a process for the vapour-phase decarboxylation of furfural using Cr, Zn and Mn oxide catalysts /217/. They have carried out the catalytic decarboxylation of furfural in the presence of steam at 115°C using a $ZnO-Cr_2O_3-MnO_2$ mixed catalyst /1 : 0,531 : 0,25/ and have attained a yield of 86,7 per cent /208/. Besides furan, CO_2 and H_2 were formed.

Sato has examined the effect of the structure and the Cr content of ZnO-CrO catalysts on the decarboxylation of furfural /218/.

Processes catalysed by metal chromites have resulted in poorer yields. On passing furfural and steam /1 : 5/ at 400° over a Mn-chromite catalyst containing K_2CrO_4, furan was obtained in a yield of only 50 per cent /219/. Zn-Fe chromite catalysts modified by 0,1 to 5 per cent. potassium or sodium ions have given similar results /220/. The process according to the Du Pont patent, working with $CuMoO_2$ or other metal molybdites proceeds also at a poor yield. A reaction mixture of steam and furfural with nitrogen as a carrier gas give over a $CuMoO_2$ catalyst only a yield of 43 per cent at a 25 per cent conversion /221/.

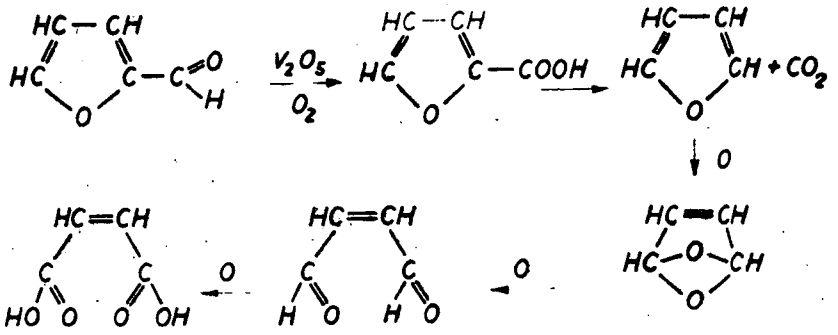
The process of Bölcs /222/ according to which furfural is treated with hydrogen in the presence of steam at 260 - 280°C appears to be of interest. A packing of pumice is used and furan is produced without the addition of any other catalyst.

Furan has been produced also from methylfuran and dimethylfuran under similar conditions.

Investigations with fluid bed catalysts have also proved highly successful. Martello and Ceccotti /209, 210/ have reduced a Zn-Mn-Cr oxide catalyst in a hydrogen stream and passed at 400°C a mixture of furfural and water vapour through the catalyst. The yield in furan was 91 per cent. The catalyst is regenerated by blowing with oxygen, followed by reduction with hydrogen.

Aliev and others have used metal alloys for the decarboxylation of furfural /211, 212/. Metal alloys offer numerous advantages over metal oxide catalysts /easier preparation and regeneration etc./Satisfactory results have been obtained with a catalyst containing 65,7 per cent of aluminium, 23,5 per cent of zinc and 10,4 per cent of iron /211/. A 65 : 5 : 3 mixture of aluminium, iron and zinc has resulted at a molar ratio of 1 : 7 to 1 : 9 furfural : water in a yield of 85 per cent.

Milas and Walsh's examinations /225/ have demonstrated that the catalytic oxidation of furfural by atmospheric oxygen with a V_2O_5 catalyst results in the formation of maleic acid. These authors present the following mechanism:



According to these authors the reaction proceeds through furan carbonic acid and furan. Tarvida, Hillers and Kalnins have also conducted thorough investigations into the vapour--phase catalytic oxidation of furfural to furan /226/ and have realized the reaction under conditions suitable also for industrial use.

The reaction mechanism discussed above, proceeding through furan, is the more likely, as besides furfural, also furan can be oxidized under similar conditions over a V_2O_5 catalyst to maleic acid. This has been proved by the process developed by Kalnins-Hillers-Tarvida /227/.

C/ INVESTIGATIONS CARRIED OUT AT THE JÓZSEF A. UNIVERSITY, SZEGED, FOR THE PRODUCTION OF FURAN

1. Melt-Bed Reactors

The survey of the described processes of possible industrial use for the production of furan points out two general methods. The first group of techniques carries out the process described by equation /1/, that is to say, the catalytic decarboxylation of furfural under the exclusion of oxygen and steam, in many cases under reductive conditions, for instance, in a hydrogen stream.

According to the second group of processes furan is produced from furfural in the presence of water vapour over a great variety of catalysts. As shown by equation /2/ this reaction proceeds through furan carboxylic acid.

Contrary to the former processes, we have developed a method for the production of furan from furfural under oxidative conditions /238-240/. Starting from the investigations of

Milas and Walsh /225/ mentioned above, who have oxidized furfural over a V_2O_5 catalyst by using atmospheric oxygen and have produced maleic acid in a fairly good yield, we have concluded that, if the reaction proceeds according to the mechanism indicated by these two authors through furan, by selecting an adequate catalyst and suitable reaction conditions, furan may be prevented from being further oxidized. Accordingly we have subjected furfural to oxidative decarboxylation with atmospheric oxygen and oxygen, respectively, without any significant over-oxydation. Our reaction, thoroughly studied, can be described by equation /3/, or, in full details, by equations /4a/ and /4b/.

A comparison of the heats of reaction of the processes represented by equation /2/ and equation /3/, respectively, shows that the heat of reaction of the oxidative decarboxylation carried out by us is significantly higher than that of the former process. Owing to the high heat of reaction the development of a number of novel-type reactors /241-244/ was necessary.

In one of the methods evolved by us, the conversion of furfural into furan takes place in a melt-bed reactor /245-250/. We have observed that in the presence of furfural, under exclusion of air, at higher temperatures lead oxide is reduced to metallic lead. Evidently, furfural is simultaneously oxidized to furane carboxylic acid. In view of the fact that lead melt is readily oxidized, an arrangement in which a mixture of furfural and air is bubbled through the lead melt appeared to be practical.

The scheme of the operation of the melt-bed reactor is shown in Figure 4. Air is introduced at the bottom into the apparatus and the lead oxide film formed at the interface of the

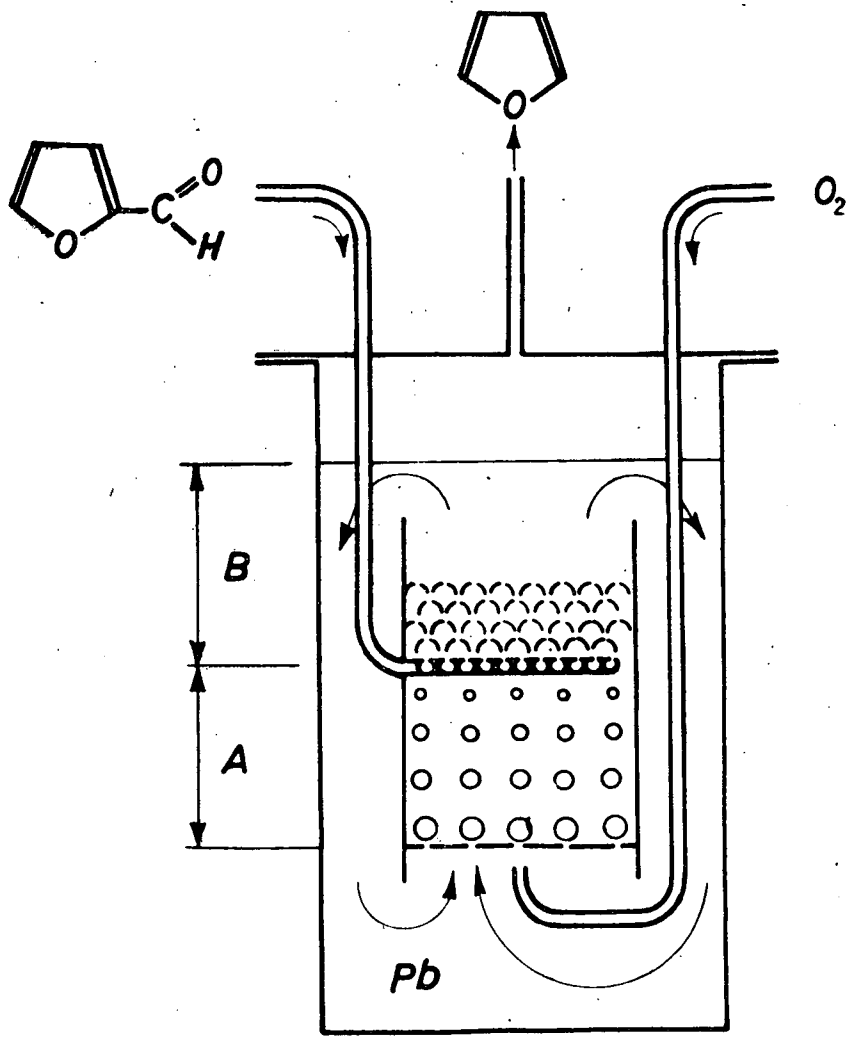


Fig. 4

air bubbles appears at the height interval "A". Gas bubble formed on the introduction of steam keep the melt in circulation.Lead oxide passing upward meets in zone "B" the furfural fed in at half height of the melt. Reaction gases are retarded on Raschig rings.Owing to this retardation there is sufficient time for the lead oxide to oxidize furfural into

furan and to regenerate by reduction to metallic lead. The reaction taking place in zone "A" is described by equation /4a/, and that in zone "B" by equation /4b/.

The bubbles can be considered as independent reactor elements. Their volume amounts to 10 to 20 per cent of the volume of the metal melt. It is very advantageous that the specific heat of lead is by three orders of magnitude higher than that of air. The close contact and the resulting high thermal conductivity render it possible to carry out the reaction under isothermic conditions.

Furan is formed from furfural by oxidative decarboxylation under conditions similar to those discussed above also if lead is substituted by bismuth. Catalytic organic processes can be carried out along the same principles also with other metals, thus with zinc, tin, cadmium, or with metal mixtures, and even with melts of non-metallic substances.

The advantageous thermal conductivity of meltbed reactors can be utilized also under incorporation of catalysts into the metal melt, provided that the melt does not react with the catalyst and does not affect in a detrimental sense the catalysed reaction. Thus, for instance, aluminium oxide submersed under the melt can be used for the dehydration of alcohols.

Our experiments and computations carried out so far show that the cross section of a melt-bed reactor can be scaled up as desired by linear computation, without the need to change the temperature or the height of the reactor. In the reactions of furan preparation the life time of the lead catalyst is very long. The contacting of air and furfural in the reactor may be arranged at variable heights, and this makes possible to establish experimentally the optimum geometrical conditions for an industrial realization.

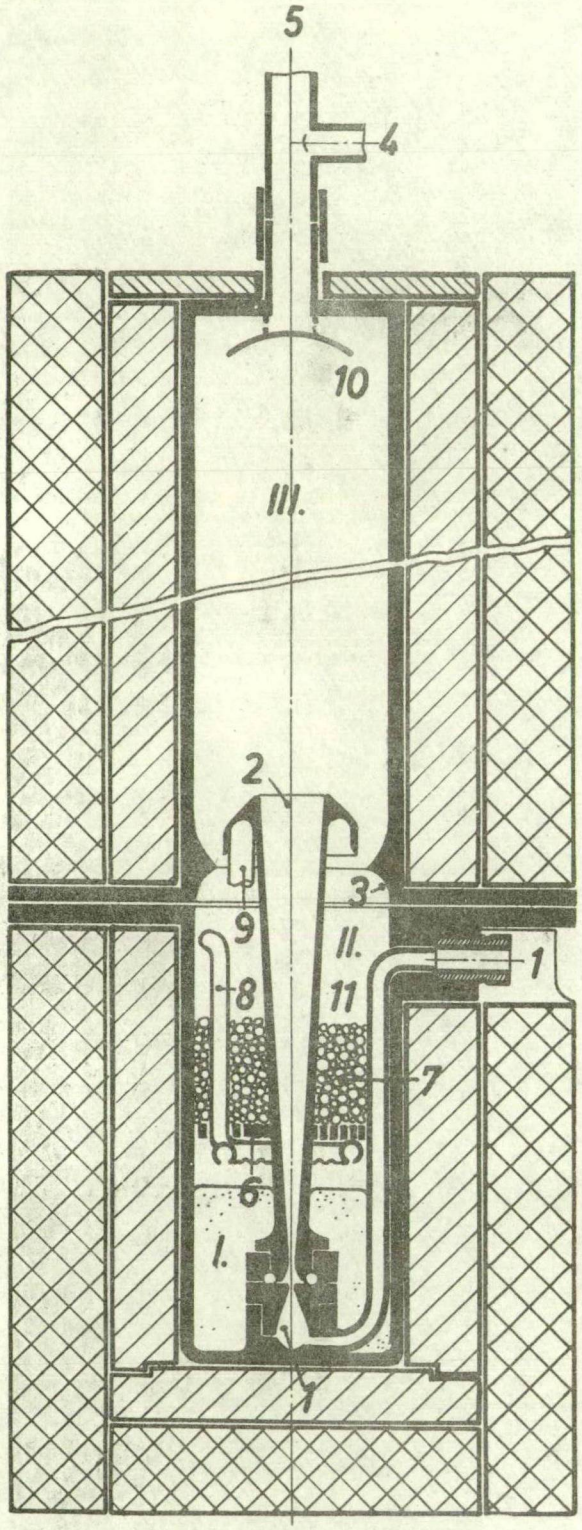
It is known that borax and glass can dissolve various metal oxides. By bubbling the substances through the melt, various reactions can be studied. Metal oxides dissolved in glass and borax, or rather their pulverized mixtures on carriers make possible the studying of classical heterogeneous catalytic processes. With reactions not sensitive to higher temperatures, various techniques like foam columns can be realized. This means a further extension of the method.

Melt-bed reactors can be used also for the classical furan production applying metal-chromite catalysts. When the metal chromites are submerged under the melt and a reaction mixture consisting of furfural and hydrogen is bubbled through the bed under exclusion of air, the known reaction resulting in the formation of furan takes place.

On summarizing the characteristics of melt-bed reactors, it can be seen that in melt-bed reactors there is less risk of local overheating than in solid-bed reactors, as not only the steam transports heat, but also the melt acting as catalyst and having a specific heat larger by three orders of magnitude than steam transports heat by convection. Since no such large contact surfaces can be produced by air dispersions as in the case of solid catalysts, the capacity of the lead melt used as a catalyst is relatively low. This drawback may be compensated by increasing the quantity of the catalyst or by applying finer spraying. A considerable advantage is that the lead melt ensures constant temperature in the course of the reaction.

2. Sprayed Melt-Bed Reactors

The sprayed melt-bed reactor /Fig. 5/ is an improved version of the melt-bed reactor. Its characteristic feature over the former model is that it works with a very small quantity of melted metal as compared to the quantity of the gas. The



I. Metal melt zone
II. Regeneration zone
III. Zone of organic reaction
1. Introduction of compressed air
2. Laval-tube
3. Flange connection
4. Introduction of furfural
5. Manipulating hole
6. Perforated ceramic plate
7. Raschig rings
8. Introduction of furfural
9. Outlet of furan gas
10. Protective screen
11. Gas outlet tube

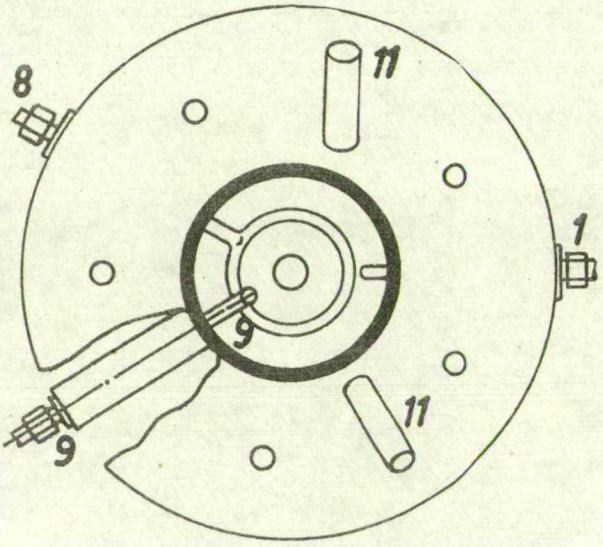


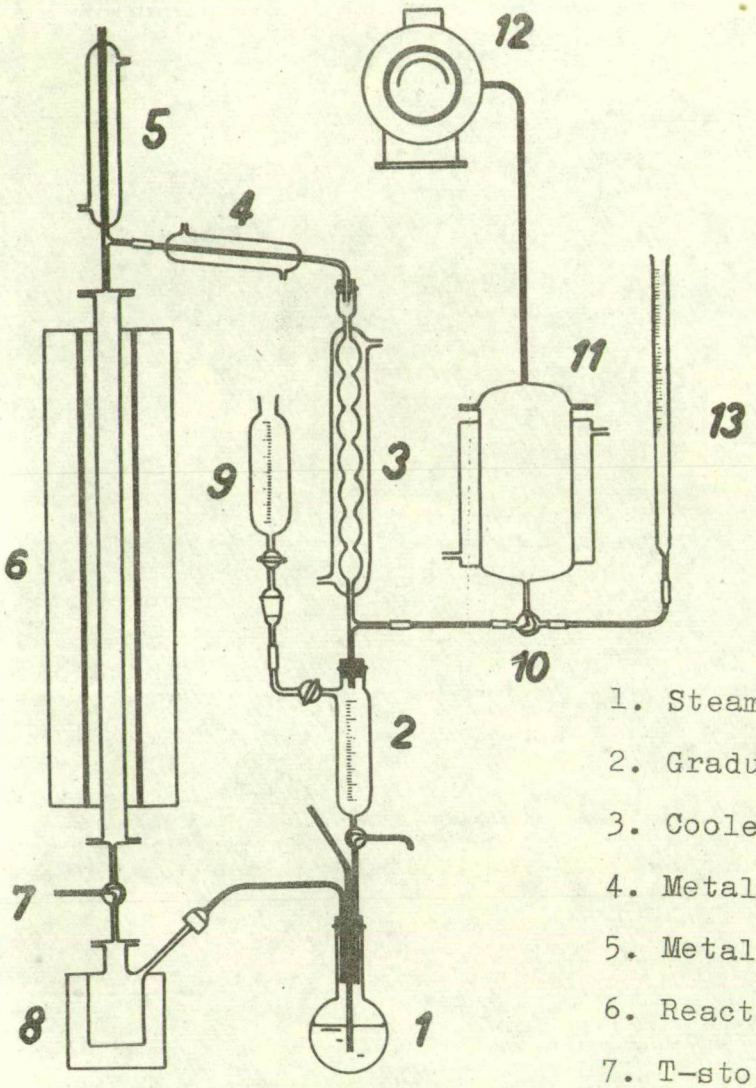
Figure 5

Sprayed melt-bed reactor

interface required for the reaction is obtained by spraying the catalyst /251/. The apparatus operates as follows: The catalyst melt is sprayed with a nozzle. In the funnel above the nozzle, analogous to zone "A" in Fig. 4, the catalyst is oxidized. Next, the metal oxide catalyst contacts the furfural and oxidative decarboxylation takes place /Zone "B" in Fig. 4/. This type of reactor can work also with a small quantity of metal melt.The formation of furan can be described by equations /4a/ and /4b/. The contact time of the lead oxide is prolonged by the use of Raschig rings.Metallic lead remains in the melt. Similarly to the melt-bed reactor, also the sprayed melt-bed reactor possesses an advantageous high thermal capacity. As spraying starts a circulation of the melt, local overheating can be prevented. From the end-gases furan may be isolated with the usual methods. This process was used by us for the production of furan both from furfural and furfuryl alcohol.

3. Reactions with Pyrophorous Lead Catalysts

The reactions taking place in melt-bed and sprayed melt-bed reactors over a lead catalyst on the effect of atmospheric oxygen can be carried out in the above mentioned reactors also under exclusion of air, if lead oxide,kept at a temperature lower by 10 - 20°C than the melting point of lead, is used as catalyst. If a lead oxide catalyst is placed into a ceramic dish /Fig. 6 and 7/, and maintained at a temperature lower by 10 - 20°C than the melting point of lead, and under exclusion of air furfural or furfuryl alcohol vapours are passed through the catalyst, furan is produced /252/. Simultaneously,lead oxide is reduced to pyrophorous metallic lead of large specific surface, which, at this temperature, can be re-oxidized by atmospheric oxygen. Care must be taken to avoid local overheating, as lead, when melted, naturally loses its pyrophorous character.



1. Steam generating flask
2. Graduated vessel
3. Cooler
4. Metal Liebig-cooler
5. Metal Liebig-cooler
6. Reactor
7. T-stopcock
8. Furfural evaporator
9. Furfural feeder
10. T-stopcock
11. Carbon adsorption column
12. Gas-meter
13. Control carbon column

Figure 6

Flow sheet of the apparatus, operating with pyrophorous lead, for the production of furan from furfural

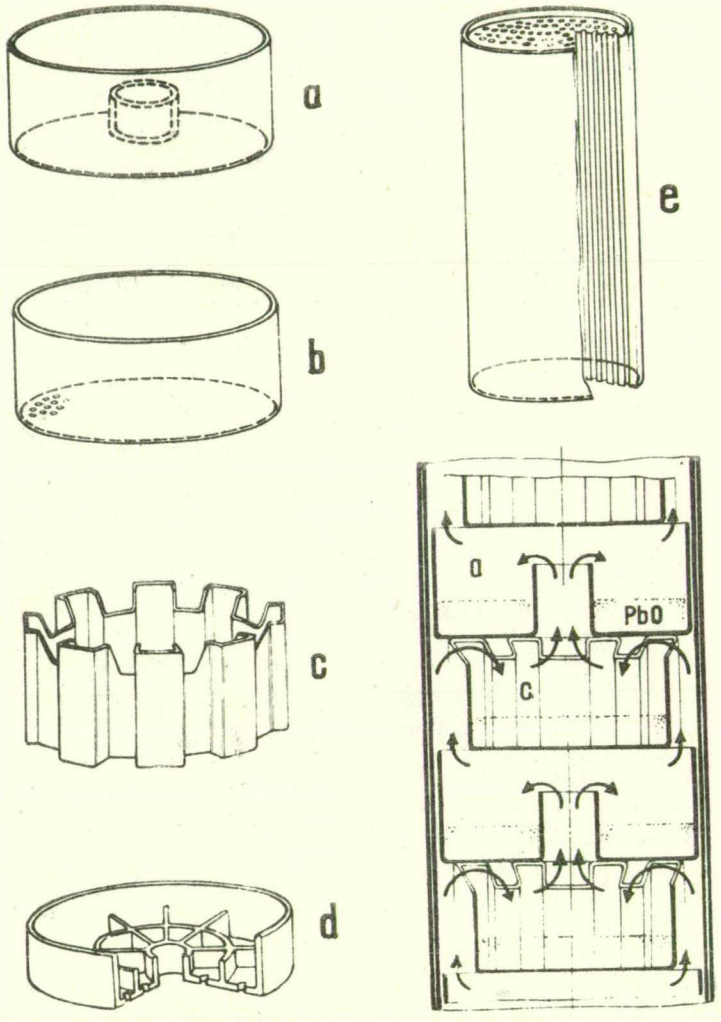


Figure 7

Ceramic dishes for supporting the catalyst

The pyrophorous character may be preserved by the use of certain additives, as alumina, titania, ceramic clay etc. The addition of these materials to the lead oxide dilutes the catalyst, reducing hereby the density of the heat source and preventing the coagulation of microscopical lead droplets possibly formed. By this method catalysts of various mechanical strengths can be prepared.

In the reactor described above /Fig. 6/ we have studied the role of water in the furfural-furan conversion. Furfural of various water content has been subjected to oxidative decarboxylation. The results have shown that the variation of the water content does not affect the percentual yield of furan. Thus, steam plays the role of an inert gas. Therefore, it is unnecessary to produce at an excess cost to industry furan free of water. Unless considerations of heat economy prevent it, also furfural wastes containing only 5 - 10 per cent of furfural may be used. By checking the amount of carbon dioxide produced in the reaction, the rate of the conversion may be kept under continuous control.

Earlier, pyrophorous lead was produced by the thermal decomposition of lead tartrate /Glistenko/. Our method permits the production of pyrophorous lead on an industrial scale. Owing to its high reactivity, pyrophorous lead is a catalyst of great importance not only in the conversion of furfural to furan discussed above and other oxydative processes, but also several other types of industrial processes can be realized in the presence of this catalyst.

As the use of pyrophorous lead as a catalyst has not been discussed in literature so far, it appears expedient to mention here some applications tested by us.

Experience has shown that pyrophorous lead is suitable for the removal of covalent halogens from organic substances in

liquid or in gas phase in the temperature range from 60 to 300°C. Radicals thus formed enter into reactions according to the Wurtz synthesis. Reactions in vapour phase can be carried out in the given reactor, or, in the case of larger molecules, in liquid phase. Organic halogen derivatives enter into reaction with pyrophorous lead at their boiling point or refluxed in an inert solvent. The formed lead chloride can be regenerated after conversion into hydroxide.

In this way we have prepared, among others, diphenylethane from benzyl chloride and benzyl from benzoic chloride. On the basis of experimental results obtained up to the present, it appears justified to consider our reaction of general validity. Under exclusion of oxygen, pyrophorous lead may be produced from lead oxide with furfural, on an industrial scale.

Pyrophorous lead proved to be suitable for use in the Wurtz synthesis instead of sodium also in the case of highly sensitive compounds, when sodium was too agressive. We hope that the use of pyrophorous lead will permit the utilization of the Wurtz synthesis also on an industrial scale.

Sprayed melt-bed lead catalysts when sludged give a metal of fine distribution. Metal fogs of the fineness of cigarette smoke can be produced by this method. There is no obstacle whatever which would hinder the automation and scaling up of the process. Pneumatic conveyance will permit the use of pyrophorous metal or metal fog in reactions on an industrial scale. Sprayed in an inert gas metals may be introduced into reactions continuously, for instance in the continuous production of organic metal compounds.

4. Mercury vapour-bed reactors

As a further development of melt-bed and sprayed melt-bed metal oxide - metal redox systems, the design of a reactor was aimed at in which both metal and metal oxide formed are of the possible finest distribution. To this end a mercury vapour-bed reactor has been developed /253-255/. The flow scheme of a mercury-vapour reactor is shown in Fig. 8.

The operation of the reactor is based on the fact that in the presence of oxygen, at a temperature of about 300°C, mercury is oxidized under optimum conditions. The formed mercuric oxide, decomposing at 400°C under evolution of 1.35 Cal of heat, is capable to deliver oxygen. Obviously, oxygen may be released also at lower temperatures, if some substance to be oxidized is present.

In essence, a mercury vapour-bed reactor is a vessel, equipped with a reflux condenser, in which mercury is boiled. The mercury evaporator is at the bottom of the reactor. The mixture of air and organic substance to be oxidized is introduced into the system above the mercury level. The temperature of mercury vapour is kept at the desired value by controlling the temperature of the reactor wall heated by electricity. In the course of the reaction first mercury oxide is formed, then the oxidative decarboxylation of furfural and the regeneration of the mercury catalyst follow. Vapours from the reaction area are led off, mercury vapour is condensed at a controlled temperature between 100 and 200°C and returned to the evaporator. As the heat of evaporation and the specific heat of mercury are relatively low, circulation can be maintained at a cost of only a small amount of thermal energy.

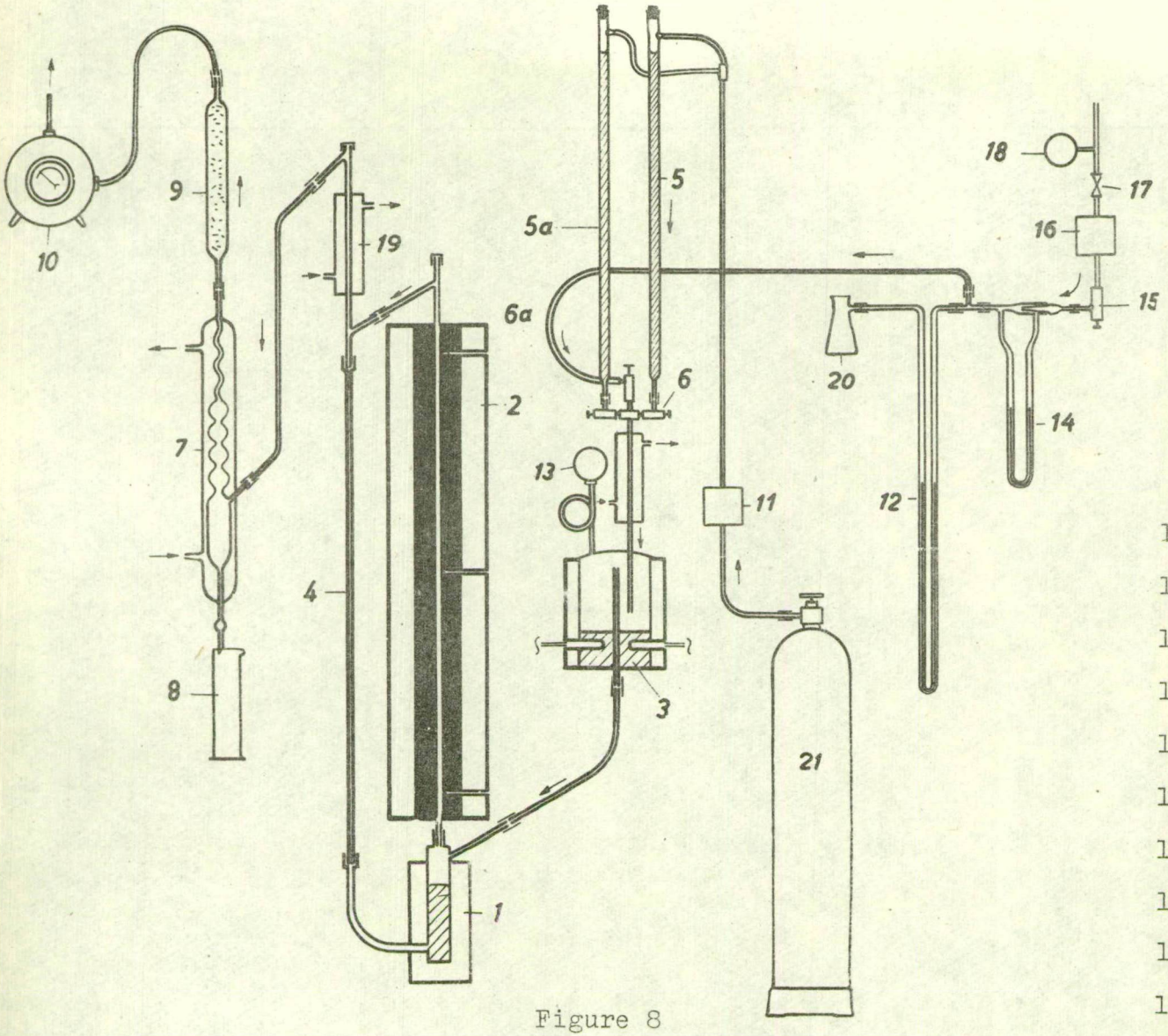


Figure 8

Flow sheet of a mercury vapour-bed apparatus
/catalyst zone: 200 ml/

1. Mercury evaporator
2. Reactor
3. Furfural evaporator
4. Mercury recirculation
5. Dosing burette
6. Needle valve
7. Condenser burette
8. Measuring cylinder
9. Carbon column
10. Gas meter
11. Reductor
12. Manometer
13. Pressure gauge
14. Differential manometer
15. Needle valve
16. Reductor
17. Valve
18. Pressure gauge
19. Mercury reflux cooler
20. Mercury trap
21. Pressure flask of inert gas

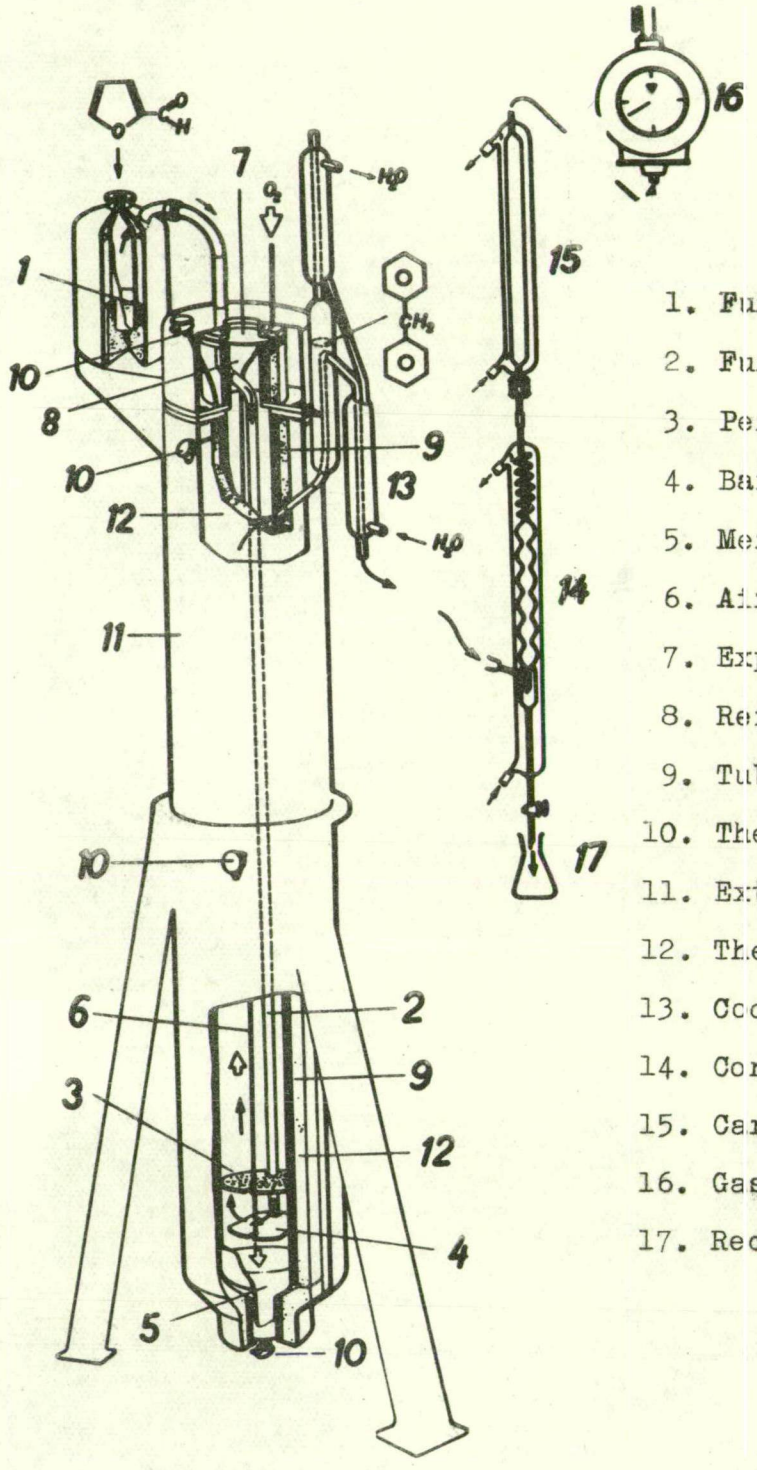
At the beginning furfural, mercury vapour, oxygen and nitrogen present in the reacting gases form a homogeneous phase. In statu nascens mercury oxide oxidizes the furfural present into carboxylic acid, which, on decarboxylation, is converted into furan while mercury regenerates. If furfural is absent, or present only in small quantities, mercury oxide fog is formed. If stirring and feed are adequate, mercury oxide will not accumulate. The process is continuous, and can be considered as a transition between homogeneous and heterogeneous catalysis.

By accelerating the evaporation rate of mercury the contact time can be reduced. This, together with the regulation of the feed rate, permits the control and even the automation of the reactor.

Our examinations have proved that Hg/HgO systems are adequate catalysts for the production of furan from furfural. They can be used also for the oxidation of toluene, benzyl alcohol and other organic compounds.

The amount of material produced by unit volume of mercury/mercury oxide catalyst in unit time, i.e. the capacity of the catalyst is relatively low. A furfural/air feed rate was determined, at which, according to calculations, the temperature of the reaction gases passing through the tube reactor is raised by not more than 15°C, by the heat of reaction. In this case, the cross section of the reactor may be scaled up as desired, as the heat exchange through the reactor wall can be neglected under such conditions.

This consideration has induced us to increase the catalyst volume of 200 ml of our reactor to 60 litres, that is to say, to threehundred times its original capacity. /Fig.9./ In this reactor, scaled up threehundred times, 450 times the former quantity of furan was obtained, which has confirmed our



1. Furfural evaporation
2. Furfural inlet
3. Perforated plate
4. Baffle plate
5. Mercury pool
6. Air inlet
7. Explosion disk
8. Reflux zone
9. Tube reactor /with heating/
10. Thermocouple
11. External jacket
12. Thermal isolation
13. Cooler
14. Condensate burette
15. Carbon column
16. Gasmeter
17. Receiver

Figure 9

Mercury vapour-bed reactor /catalyst zone 60 litres/

assumption. The increase of the specific production to one and a half of the former value is probably due to the fact that the negative catalytic effect of the reactor wall coated by iron-oxide prevails to a smaller extent when the dimensions of the apparatus are larger.

Our computations and also other experiments induce us to believe that this principle represents a principle of scaling up that can be generalized. /256/. Thus, reactors operating at low capacity may be enlarged. When using inexpensive catalysts, this permits the realization of industrial plants along the same principle.

5. Plane-Parallel, Disk and Spherical Segment Reactors

In the scaling up of reactors various parameters are to be expected to change. With the changing of the ratio of reactor wall to catalyst volume, heat dissipation changes and this affects the rate of reaction and the yield. With reactors of older types a possible local overheating along the axis is of special importance. The alteration of the mixing conditions of the reaction gases means a similar drawback.

On scaling up a reactor, the main difficulty is caused by the formed and disappearing heat of reaction, i.e. by heat exchange proper. Reactors can be scaled up correctly when no essential changes take place in the ratio of heat exchange surface to catalyst area, and other similarity factors.

Let the length of a reactor tube of optimum operating condition be l, and its radius r_2. In this case the catalyst area per unit of heat exchange surface is $r/2$ cm^2. If this ratio is not changed, a plane-parallel reactor /Fig.10/ or a disk reactor /Fig. 11/ can be constructed, the height, or the diameter of which is l and its wall thickness r.

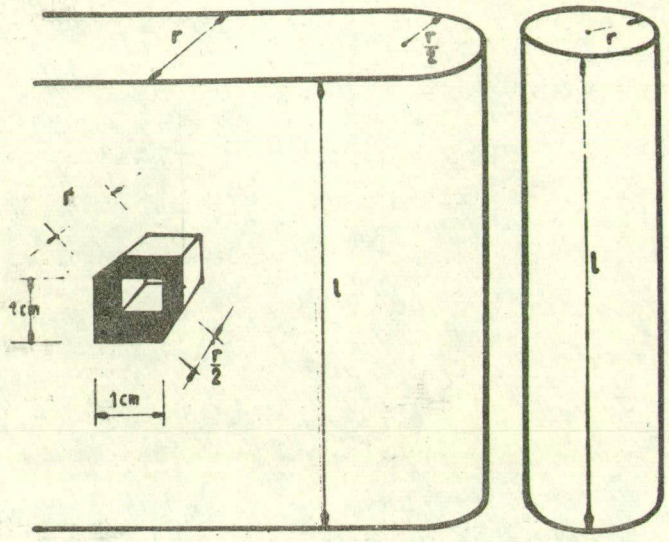


Figure 10
Schematic diagram of the plane-parallel reactor

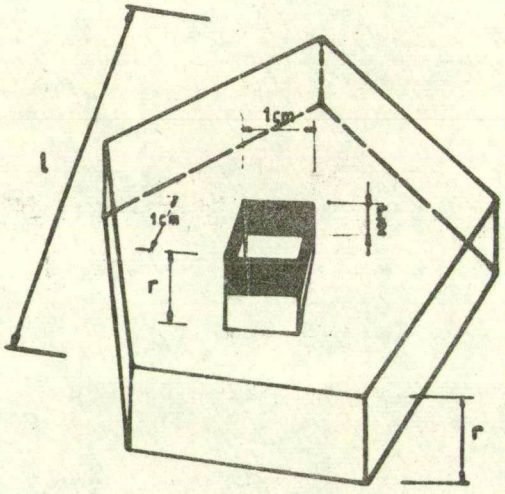


Figure 11
Schematic diagram of the disk reactor

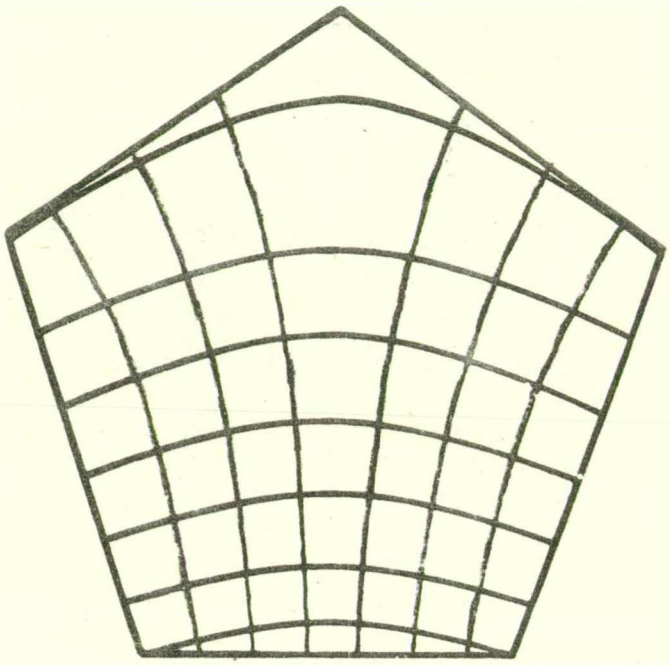
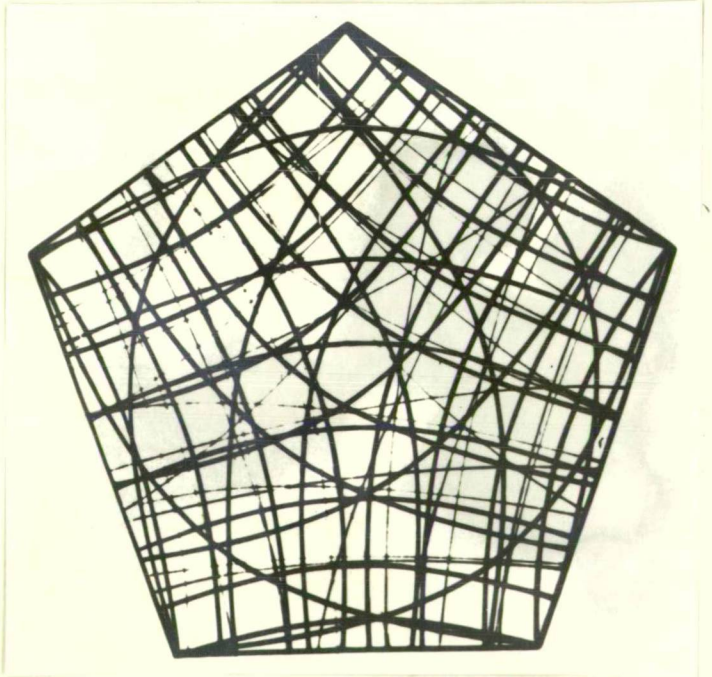


Figure 12
Distribution of ammonia vapours in the disk reactor



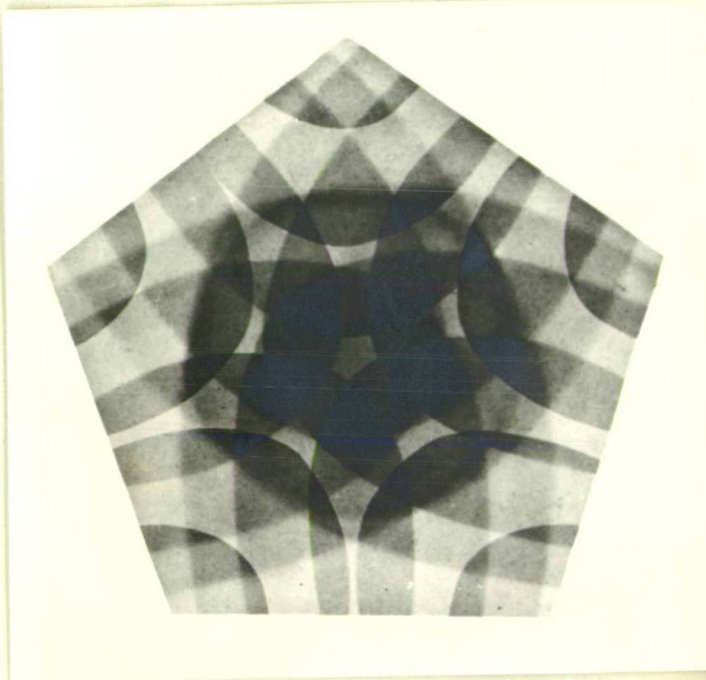
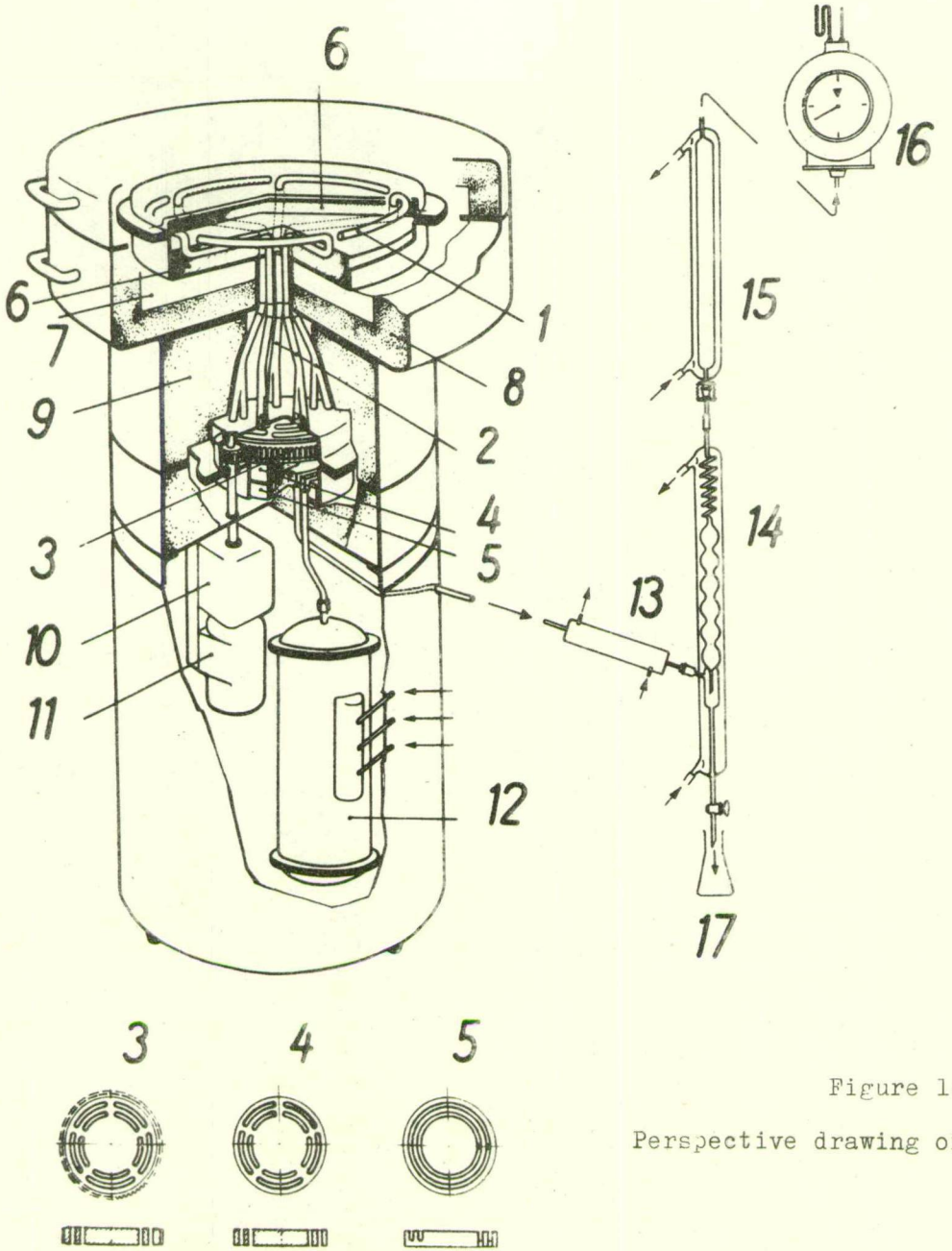


Figure 13
Distribution of ammonia vapours in the disk reactor



1. Perforated gas inlet and outlet tubes
2. Y-form gas outlet pipes
3. Parts of the gas distribution head of the control gear
4. Parts of the gas distribution hand of the control gear
5. Parts of the gas distribution head of the control gear
6. Catalyst zone
7. Heating ceramics
8. Heat insulation
9. Heat insulation
10. Speed reducing gear
11. Motor
12. Evaporator
13. Metal Liebig-cooler
14. Condensate burette
15. Carbon adsorption column
16. Gas meter
17. Receiver

Figure 14

Perspective drawing of disk reactor

Aiming at the development of a disk reactor that can be used also for production, we constructed a glass reactor, into which air containing ammonia was introduced and withdrawn at various points. The ammonia vapours coloured filter paper moistened with phenolphthalein. Thus the distribution of ammonia vapours introduced at various points could be studied. The distribution of ammonia vapours introduced in succession at the various inlet points was studied on this model /Figs. 12 and 13/.

On presuming that equithermal surfaces are formed in a similar way, a disk reactor has been designed /267/, /Fig.14/. A control gear with variable time period changes the inlet and outlet points of the reaction gases. Vapours leaving the evaporator enter the catalyst area through a bent perforated tube and leave through the selected outlets, generally through those facing the inlets. Number, location and time programme of the feed tubes can be selected in advance. During one period the reacting steam is uniformly distributed on the surface of the solid catalyst in the disk and this prevents the local overheating of the catalyst.

In order to facilitate the technique of scaling up, spherical segment reactors and spherical reactors have been constructed.

D/ S U M M A R Y

In the Introduction a survey of recent literature on the structure of furan and the most important chemical characteristics of furan and furan derivatives have been given. The aromatic reactions of furan, the use of furan derivatives in diene synthesis, reactions involving the cleavage of the furan ring have been discussed. The hydrogenation of furan and derivatives has been described. The syntheses of some nitro compounds starting from furan, and the use of furan and derivatives in the plastics industry have been outlined.

Several variants of industrial furan production have been discussed in detail. Processes of producing furan from furfural by the Cannizzaro reaction, by decarboxylation and by other methods, described in scientific and patent literature, have been dealt with in detail.

Novel type reactors developed by the author and co-workers at the József A. University, Szeged, have been described. These reactors, constructed for the oxidative catalytic decarboxylation of furfural lend themselves also to carrying out other oxidation reactions. Melt-bed, sprayed melt-bed, pyroforous lead and mercury vapour reactors designed by the author and coworkers have been described. Experiments and calculations concerning the scaling up of reactors have been carried out. Scaling up is free of problems in the case of plane-parallel and disk reactors.

For the synthesis of furan from furfural methods suitable also for industrial application have been developed. Our reactors, designed according to new principles, may be used for conducting and investigating a number of other processes /152, 262-263/. As a result of our experiments further points in the reaction mechanism of furan formation have been elucidated and new methods and principles, of general use in reactor chemistry have been developed.

x x x

In conclusion we wish to point out that the equipment shown in Figures 1 to 4 form but a part of the catalytic laboratories, developed so far and used in the research and training work of the József A. University, Szeged. This equipment is a great help in the systematic research work carried out in the field of vapour-phase catalytic reactions, in the examination of catalysts and in other branches of scientific and industrial research. The equipment facilitates the training of students in chemical engineering /258-261/. In most of the cases, students do not work on the reproduction of experimentally established processes, but are engaged in the systematic investigation of reactions to be cleared up. Consequently, besides gaining experience in research work, students feel greater responsibility and their ambition increases.

I wish to thank the Factory for Laboratory Equipment /Budapest/ and Metrimpex /Budapest/ for giving to our University one of each type of equipment developed by us and manufactured now in series by the Factory for Laboratory Equipment. This present of a value of several millions of forints has helped to raise the level of our educational and research work.

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Part II.

CHEMICAL AND PHYSICAL FUNDAMENTS PERTINENT TO THE EXPERIMENTS

Catalysis in general. The role of interfacial phenomena in the conversion of furfural to furan

A/ FUNDAMENTALS OF CATALYSIS

1/ Definition

Catalysis is the alteration of the rate of chemical reactions on the effect of an added substance of relatively minute quantity. This substance, the catalyst, without being consumed, opens up new paths for the reaction, which, while thermodynamically possible, do not proceed spontaneously.

When generally representing the course of a chemical reaction, the effect of the catalyst may be symbolized as follows:

Non-catalytic reaction: $A + B \xrightarrow{K_1} AB$

$$A + \text{catalyst} \xrightarrow{K_2} A - \text{catalyst}$$

$$A - \text{catalyst} + B \xrightarrow{K_3} AB + \text{catalyst}$$

The catalyst forms an intermediary compound with one of the reaction partners and on further reaction, results in product AB, and the catalyst is reformed. The rate of a homogeneous catalytic reaction depends on the rates of formation and decomposition of the intermediary compounds.

A catalytic process is denoted as heterogeneous when the catalyst is not in the same phase as the reacting system. In this case the intermediary product is formed on the surface of the catalyst. Besides by the proper chemical reaction, the rate of heterogeneous catalysis is influenced also by the rates of sorption and desorption.

Depending on whether the catalyst increases or decreases the rate of reaction, catalysis can be positive or negative, independently from the fact whether the effect of the catalyst is due to a chemical or a physical process.

2/ Effect of catalysts on the activation energy

It is known from physical chemistry that in the course of a bimolecular reaction between two compounds, A and B, only a small fraction of the colliding molecules enter the reaction. The rest of the collisons are ineffective.Only a part of the molecules in the system possess the necessary activation energy.

$$A \rightleftharpoons A^{+} \quad ; \qquad {}^{+}A = \text{activated molecule}$$

With a rise in temperature, the rate of the reaction also increases as a higher percentage of the molecules becomes activated. An equation giving the dependence of the reaction rate on temperature was derived by Arrhenius:

$$K = A \cdot e^{-\frac{E}{RT}},$$

where K is the rate constant,

A is an action constant or pre-exponential factor, and

$\frac{E}{RT}$ is Boltzmann's constant

In several cases substantial deviations from Arrhenius' equation were observed and the introduction of a so-called steric or probability factor "p", has proved necessary

$$K = pA.e^{-\frac{E}{RT}}$$

There are cases when the number of activated molecules increases not as a consequence of a rise in temperature, but due to the "catalytic" effect of some additive, causing the reaction to proceed in a different way, as, for instance, in the case of enzyme-catalysed reactions. It follows from the study of the energy profile that in a catalytic process the activation energy decreases /Fig. 15./.

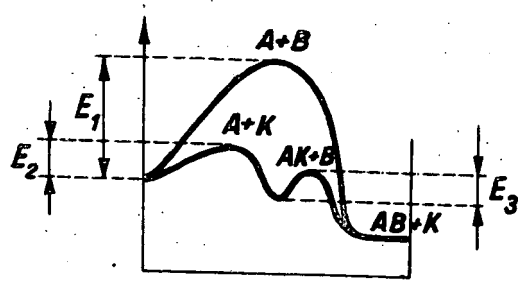


Figure 15

The trend of activation energy in catalytic processes

The values of activation energies in the general process mentioned above in the presence or absence of a catalyst, are the following:

$$A + cat. \rightleftharpoons A - cat. \qquad E_2$$

$$A - cat. + B \longrightarrow AB + cat. \qquad E_3$$

and

$$A + B = AB \qquad E_1$$

$$E_2 + E_3 < E_1$$

The causes of the decrease in activation energy could not be cleared up so far. It is, however, a fact that adsorbed vapours are easier to activate than non-adsorbed vapours. Thus, for instance, on a Pt surface a H_2 molecule will dissociate to H atoms at a small energy input. Electrostatic forces on the surface deform the molecules entering the active field, quasi loosening the bonds, and this may cause a

significant decrease in activation energy, or, in an extreme case, its complete cessation.

3/ Dispersity and activity of catalysts

Heterogeneous catalysis, brought about by whatever cause, in the first step is directly connected with adsorption. It can easily be seen that the activity of a catalyst firstly depends on its surface area. The larger the surface of the catalyst and the easier accessible, the higher is its catalytic activity. The surface area of a catalyst may be characterized by its specific surface, that is: the surface area of the catalyst per unit weight. With highly porous substances specific surfaces can reach extremely high values.

Catalytic activity is a function of the chemical properties, structure, specific surface and surface morphology of the catalyst. The sites of highest activity on the surface of catalysts are the submicroscopical edges and peaks. Crystal cracks contacting surfaces of two solid phases or crystal defects represent further active points. Sometimes the addition of a minute quantity of an inert substance may suspend the catalytic activity /catalyst poisons. For details see Part II Paragraph A/10/. Submicroscopical cracks may easily fill up, and thus do not play a considerable role in catalysis. The important activating action of edges and peaks is shown also by the fact that on increasing the degree of dispersion of the catalyst, catalytic activity increases at a higher rate than the surface.

From all this follows that, among otherwise identical substances, those in colloidal state have the highest catalytic activity. Colloidal substances have the highest specific surfaces and the highest number of submicroscopical edges and peaks. This proves the great importance of the microstructure of catalysts. In order to increase the surface of the catalyst, various carriers are used. Substances named

skeleton catalysts, having complicated cross-linked structures advantageous for catalysis, display a high activity and play an important role.

4/ Role of the quantity of the catalyst in heterogeneous reactions

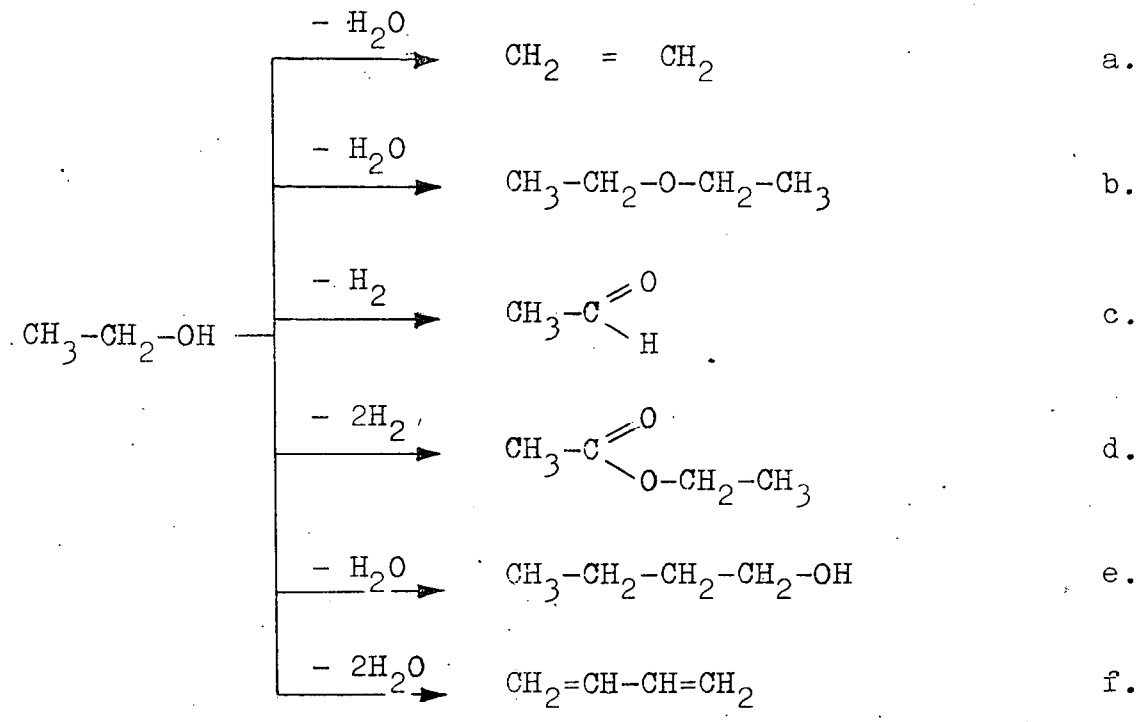
In the course of application of individual catalysts, results concerning their selectivity could be attained by varying their quantity. It has been found that the reaction rate generally increases with an increase in the quantity of the catalyst. Stepf, and later Daniel observed that in some conversions there is a minimum quantity of catalyst under which threshold value no reaction starts. Kailan and Hartal established in 1937 that an increase in the quantity of the catalyst increases the rate of reaction up to a certain limit, beyond which the rate of reaction decreases again.

Similar results were obtained by Csürös and co-workers who on varying the quantity of catalyst obtained curves passing through small local minima and maxima. The examination of a number of hydrogenation and oxidation reactions has proved that in some cases the variation of the quantity of catalyst is sufficient to render the reaction selective. Selectivity thus obtained may be explained by the fact that the change in rate of consecutive or parallel reactions with the variation of the quantity of the catalyst is different. The predominance of one of two or several reactions depends on the ratio of the partial rates. In a favourable case, the rate of one of the reactions may show a maximum just with a catalyst quantity where the rate of the other reaction shows a minimum. It can be seen that the quantity of catalyst is of paramount importance with heterogeneous catalytic reactions, as there is a relation between rate constant, order of reaction and the quantity of catalyst.

5/ Selective catalysis

In the case of chemical conversions in which thermo-dynamical equilibrium may be established through different intermediary steps, there is a possibility to stop the reaction at an intermediary step and to obtain different products depending on the quality of the catalyst. The isolation of the intermediate products becomes possible by the fact that the rate of only one or some of the partial processes is selectively accelerated by the catalyst. Selectivity is most characteristic for enzymes which, in most cases, catalyse only a single reaction, i.e. their action is specific.

Catalysts used in practice usually not only accelerate or slow down the process, but in cases when in course of a reaction different products may form, only one of the rate of formations is altered decisively by the catalyst, resulting in an increase in the percentage yield of the desired end product at the cost of the by-product. Selective catalysis is of paramount importance in the syntheses of various industrial basic materials. As an example some of the possible conversions of ethanol are shown:



Every reaction is accelerated by a specific catalyst. Ethylene may be prepared by passing ethanol over an Al_2O_3 catalyst or treating it with sulphuric acid at 200°C. Diethylether is obtained with the same catalysts at 250 and 140°C, respectively. Acetaldehyde is produced by dehydrogenation over Cu at 200 - 250°C while with another Cu catalyst ethyl acetate is obtained. Over alkaline catalysts butanol is formed and the use of $ZnOCr_2O_3$ catalyst results in butadiene. By utilizing the selectivity of catalysts the processes may be directed in the required direction. The choice of the best suited catalysts and conditions is, of course, a most difficult task, as neither the causes of the selectivity of catalysts, nor the theory of catalysis have been sufficiently cleared up so far.

6/ Influence of temperature on catalysis

In catalytic processes the rate and in many cases also the direction of the reaction, further the life of the catalyst and its activity depend on temperature. In a given reaction

and other parameters being constant, catalysts show maximum effect at sharply defined temperatures.The higher the activity of the catalyst, the lower is this temperature, and limited to a narrower interval. The rise of temperature, therefore, besides increasing the reaction rate by about two or threefold for every $10^{\circ}C$ - exact numerical relationships being given by the Arrhenius equation - may also destroy the catalyst or reduce its activity, if the optimum temperature of the catalytic reaction is exceeded. This is why in carrying out the reactions, particularly exothermic processes, temperature fluctuations and overheating cannot be permitted.

The selectivity of catalysts may be improved in some reactions by the application of the Le Chatelier's principle, as the selection of the conditions for the reaction can be made in consideration of the fact that a rise in temperature slows down the exothermic and accelerates the endothermic reactions.

7/ Effect of pressure on catalysis

In accordance with the Le Chatelier-principle also pressure influences significantly the direction of the conversion. A decrease in pressure will be favourable to processes proceeding with an increase in volume, while the increase in pressure will promote reactions accompanied by a reduction in volume. Corresponding to this, the synthesis of methanol from CO and hydrogen, syntheses of hydrocarbons from CO and hydrogen, and the synthesis of ammonia from nitrogen and hydrogen etc. take place more readily under high pressures.

On the other hand, processes proceeding with an increase in volume, as, for instance, dehydrogenation, give higher yields at lower pressures. The major part of catalytic processes can be carried out also at atmospheric pressure, in a number of cases, however, overpressure is needed.

Generally, also the reaction rate of processes not accompanied by changes in volume increases with higher pressures, as pressure increases the number of effective collisions.

8/ Space velocity, contact time

In case of homogeneous reactions the catalyst is evenly distributed in the system. Heterogeneous reactions are assumed to occur only on the surface of the catalyst. The degree of conversion in a given system is determined by the ratio of the quantity of the catalyst and the feed rate. Space velocity is the ratio of the volume of gas introduced in unit time /usually in an hour/ to the volume of catalyst.

$$\text{Space velocity} = \frac{B}{V_k},$$

where

B = Feed rate of the gas mixture

V_k = Volume of catalyst

When calculating the space velocity of reactions carried out under pressure the gas must be reduced to normal conditions.

Contact time is another important factor in heterogenous catalytic reactions. It is defined as the residence time, expressed in seconds, of the gas or vapour in the reactor and is equal to the reaction time. In the knowledge of the dimensions of the catalyst tube, contact time may be calculated directly from the flow rate through the reactor tube, provided that the volume of the reaction mixture does not change in the tube reactor.

Space velocity and contact time are fundamental factors in heterogeneous reactions, since they influence considerably the rate of reaction and the yield of products.

9/ Aging and regeneration of catalysts

The examination of the activity of catalysts as a function of time shows three distinct phases. In the first phase

- which often is an induction period of considerable length - catalytic activity is rather low, then it gradually increases until a constant activity level is reached. This may be considered as the beginning of the second period. In this phase the catalyst exerts its action on the process for a longer time at constant activity. The third phase is the gradual exhaustion of the catalyst, which may be due to the deformation of its surface, the degradation of sites of higher activity, possible deposition of products of higher molecular weight or changes in structure owing to local overheating.

The changes occurring during the aging of catalysts have been studied by several research workers. In a number of cases the decrease of the surface area could be established. The life of catalysts, depending on various external conditions and on the purity of reagents, may range several weeks or months, or even longer.

In many cases a catalyst which has lost its activity may be regenerated. The methods of regeneration vary in dependence of the catalyst. Spongy platinum, for instance, may be regenerated by blowing through it oxygen. The removal by oxidation of substances deposited on the surface of catalyst is a technique often used also with other catalysts. In practical regeneration, primarily the particular properties of the given catalyst are to be taken into account.

10/ Catalyst poisons

Catalyst poisons are substances which reduce or destroy the activity of catalysts. Catalyst poisons may be solids, as Pb, Cu, Mg, arsenates, cyanides; liquids as Hg, H_2O, C_2H_5OH; and gases as CO, CO_2, H_2S, Cl_2, water vapour etc. Their effect may be violent, moderate or weak, and the poisoning produced may be reversible or irreversible.

The effect of poisoning may be characterized by the poisoning coefficient, the numerical expression of the effect of a specified quantity of poison on a specified quantity of catalyst.

Its value is given by the following equation:

$$K_c = K_o/1-a.c/$$

where:

a = poisoning coefficient
K_o = rate constant of reaction for concentration c of the poison
c = concentration of the poison
K_o = rate constant of reaction in absence of the poison.

Generally, in cases of poisoning tests carried out aim partly to establish the quantity of poison which leads to the complete inactivation of the catalyst, and partly to determine the strength of the bond between catalyst and poison, that is to say the value of the endurance factor, on which the possibility of the regeneration of poisoned catalyst depends. The change of the poisoning effect with temperature has been studied. It was found that within a certain temperature range, the increase in temperature does not alter the rate constant of the poisoning catalytic reaction. On the other hand, increase of pressure intensifies poisoning.

The examination of numerous poisoning mechanisms has proved that the poison enters into reaction with the active centres of the catalyst, occupying first of all the sites of highest activity. Consequently, the catalyst is inhibited in exerting its reducing action on the activation energy of the reaction to be influenced.

11/ Effect of promoters on catalysts

Up-to-date catalysis techniques make wide use of the increase in activity of catalysts brought about by the addition of various substances. As a result of thorough investigations Taylor has found in numerous instances that the addition to the catalyst of a substance, which by itself has no effect on the reaction, may improve the activity of the catalyst /promoter effect/. In other cases, two substances used separately as catalysts, when applied together, were found to be of much higher efficiency than of either of them alone, due to co-activation. /For instance, an Fe-Mo mixture used in the synthesis of ammonia, and Fe and Mo, respectively./ These co-activated catalysts are called also mixed catalysts.

The mechanism of this promoting action has been investigated in detail. It has been established that an optimum effect is to be obtained at a certain ratio of catalyst and promoter /activator/. It is assumed that in cases when the catalyst is capable of forming an intermediate compound, the promoter accelerates both the production and the decomposition of the intermediate complex. Two kinds of promoter effects can be distinguished:

a/ structural promoting effect
b/ synergetic promoting effect.

Structural promoter effect consists in the prevention by the promoter of the formation of larger aggregates of active centres, for instance, in ZnO catalysts rich in Cu, ZnO protects CuO from forming larger aggregates after reduction. Synergetic promoter effect is attributed to the important role played by forces active on the phase boundaries /e.g. ZnO, CuO/ in catalytic activity.

The action mechanism of the promoter effect has been thoroughly investigated and the results obtained give valuable help

in selecting and using activators. A comparison of activators and catalyst poisons shows that activators are mostly metal oxides or salts from which oxides are formed. They usually have a high melting point and exert a stabilizing effect on the structure of the basic catalyst. In addition, they cause structural changes resulting in the formation of active centres and in a higher geometrical symmetry. The majority of promoters crystallizes in the regular or in the hexagonal system. Contact poisons, some types of which have already been mentioned, usually belong to the rhombic or trigonal crystal class. Most probably these influence the activity of catalysts because of the absence of symmetry elements and because of their high adsorptivity, reducing or suspending hereby the catalytic activity by the possible formation of stable compounds.

17/ Catalyst carriers

Catalysts often are supported on some material of high porosity. Such materials are called carriers, and catalysts thus prepared are catalysts supported by carriers. When selecting a carrier, its nature and characteristics must be carefully considered. Important factors needing attention are chemical composition, grade of dispersity, physical condition of the surface, the quantity of the catalyst to be applied to the carrier surface and the ratio of catalyst to carrier. The characteristics of a catalyst often change when supported by a carrier, due probably to the interaction between the electron systems of carrier and catalyst. The details of this problem have not been cleared up yet.

13/ Methods for testing catalysts

The catalyst best suitable for a particular reaction is still selected on an empirical basis. Experimental work may be facilitated by using available knowledge. The general cha-

racterization of catalysts may begin by the measurement of physical properties. In the first place the relationship between surface area and activity is examined. For this purpose the density and porosity of the catalyst are determined as characteristic values. In respect to crystal structure X-ray diffraction, to surface crystal structure electron diffraction analysis, and to microstructure electron microscopy may furnish valuable and characteristic data /see Part III, E/. In many cases the examination of the magnetic properties of the catalysts may give interesting, useful informations. The measurement of gas and vapour absorption on the catalyst, generally carried out by volumetric and gravimetric methods, is also of importance. Data obtained by physical measurements may substantially contribute to a better understanding of catalyst properties, but the suitability of a catalyst for a certain purpose, that is to say, the actual influence of the prepared catalyst on the given reaction, may be established only by practical tests.

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B/ EFFECT OF INTERFACIAL PHENOMENA ON CATALYTIC GAS REACTIONS, IN PARTICULAR CONSIDERATION OF THE CONVERSION OF FURFURAL TO FURAN

Interfacial phenomena play in two instances a decisive role in the studied process:

a/ adsorption proceeding on the catalyst or on the oxydizing agent /e.g. on lead oxide/ influences the reaction mechanism of the process,

b/ furan formed in the course of the reaction is recovered by vapour adsorption from the final mixture.

Fundamental knowledge relating to these two fields will be discussed in the following.

1/ Effect of adsorption on gas reactions

Generally, adsorption can affect chemical processes in two ways:

a/ It alters chemical equilibrium;
b/ it alters the rate of reaction.

Numerous examples for these two effects, both of great significance in practical work, are met in gas reactions.

a/ Alteration of the chemical equilibrium due to adsorption

In the presence of an adsorbent the chemical equilibrium always shifts in favour of the compound absorbed to a higher extent. As compounds of higher molecular weight /less volatile/ are adsorbed to a higher extent, adsorption always promotes the formation of compounds of higher molecular weight. For instance, in a system composed of ammonia, nitrogen and hydrogen, in the presence of an adsorbent, more ammonia is in equilibrium with nitrogen and hydrogen in the adsorption layer, than in a free gas zone.

b/ Alteration of reactivity due to adsorption /Heterogeneous catalysis/

Heterogenous catalysis may be due to several causes. These may be present also simultaneously and interact to strengthen or weaken their influence on the reaction rate. These causes are the following:

Increased concentration in the adsorption layer. Since in the adsorption layer the concentration of reactive molecules is higher than in the gas phase, the rate of the reaction will also be higher in this layer than in the gas phase. As compared to other factors, this factor plays a relatively unimportant part.

Lengthening the contact time of the molecules participating in the reaction. Owing to adsorption the contact substance /catalyst/ keeps the molecules participating in the reaction for a relatively longer period in the vicinity of one another. This increases the number of molecules entering into reaction with one another without being previously brought into the otherwise necessary activated state /"tunnel-effect"/.

Energy transfer. The energy released in the course of the reaction is carried away by the catalyst preventing hereby the decomposition of the product.

Oriented adsorption. Molecules of asymmetrical structure are adsorbed with a definite orientation. Owing to this, the parts of the adsorbed molecules directed towards the gas phase are in a more favourable position as regards the reaction than molecules in the gas phase. When these parts of the molecules directed towards the gas phase participate in the reaction, the catalyst increases the rate of reaction ·/positive catalysis/, while those parts of the adsorbed molecules which are directed towards the surface of the adsorbent are quasi pro-

tected from meeting the molecules in the gas phase. If, on the other hand, these parts participate in the reaction, the contact substance slows down the rate of reaction /negative catalysis/.

Formation of nuclei. With gas reactions where either an intermediary or the end product is a liquid or a solid adsorption may increase the rate of reaction because small traces of the product constituting the new phase formed in the adsorption layer act as nuclei, similarly to nuclei formed in condensation or crystallization.

Formation of intermediate compounds between the contact substance and the substrate /decrease in activation energy/. According to conception of long standing, catalysis is essentially based on chemical interactions. One of the reactants reacts at a high reaction rate with the catalyst and a low activation energy is already sufficient for the resulting product to react at a high reaction rate with the other reaction partner /see Part II, Paragraph A/2/.

According to the latest researches on reaction mechanism, this theory has become actual again in an up-to-date form. A chemical reaction can take place only if the individual atoms or the groups of atoms of the molecules undergoing changes or entering an interaction with one another detach themselves from one another and combine in a different grouping to molecules of the reaction product. The energy necessary for the rupture /dissociation/ of atomic bonds and for the rearrangement of atomic groups is partly or entirely covered by the so-called activation energy. In non-catalysed reactions, activation energy is usually supplied by thermal energy supplied to the system. In the presence of a catalyst, less thermal energy is needed to bring about activation, which means that the catalyst reduces the activation energy. This may be explained as follows:

The contact material as an adsorbent adsorbs one or all components of the reaction. Surface forces deform the adsorbed molecules, critical bonds in respect to the reaction are loosened, i.e. the molecules become more or less activated. As a consequence, in order to attain a fully activated condition less thermal energy is required than in gas phase. This is the cause of the increase in the rate of reaction.

The energy required for the deformation of adsorbed molecules and for the loosening of the bonds, i.e. for partial or full activation is supplied by the heat of adsorption released in the course of adsorption. As a first approximation it may be said that the catalyst reduces the activation energy of a non-catalysed reaction by the value of the heat of adsorption.

2/ Effect of the surface structure of the contact substance on its catalytic activity

Considering that heterogeneous catalysis, due to any of the various factors, is always connected with adsorption, it becomes evident that all factors influencing the adsorptivity of the contact substance, are decisive also for its catalytic action. Strictly speaking one should speak about chemisorption, as the significant increase in the reaction rate of catalysed reactions and often also the influence of catalysis on the direction of the reaction cannot be explained solely by physical adsorption. Catalysis means a radical intervention in the reaction and the catalyst participates in the intermediate reactions. It is evident that catalytic efficiency greatly depends on the surface area of the catalyst. The larger the surface of the contact substance and the easier accessible, the higher is its efficiency as a catalyst. Thus, similarly to the adsorbents, one of the principal characteristics of contact substances is their large specific surface.

The adsorbtion capacity is characterized by the specific adsorption, that is to say by the quantity of material adsorbed by unit surface/1 sq.cm/ of the adsorbent. Similarly, the activity of a catalyst would be represented most accurately by the activity of the unit surface of a contact substance. The specific surface of catalysts, however, cannot be precisely determined in every case. Expediently, therefore, the catalytic activity of the unit mass of the catalyst will be used in the comparison of the catalytic activity of various contact substances. The catalytic activity of the unit mass of a contact substance is called specific catalytic activity. Numerically it is characterized by the ratio of the reaction rate constants, $\frac{k_m}{k}$, where k_m is the rate constant of the catalysed reaction, when 1 litre of the system contains 1 g of contact substance, and k is the rate constant of the same non-catalysed reaction proceeding under otherwise identical conditions.

The quantity of gas adsorbed by 1 g of adsorbent /relative specific adsorption/ depends not only on the quality and on the specific surface of the adsorbent, but also on its morphological characteristics /radius of curvature, surface roughness/. Similarly, the specific catalytic activity is a function also of the chemical properties of the contact substance, its specific surface and the morphological characteristics of its surface. Also in this respect a far-reaching parallelism exists between adsorptivity and catalytic activity. As regards adsorption, surfaces rich in edges and peaks, and particularly those displaying submicroscopical roughness, are the most active adsorbents, because the free energy of atoms present on edges and peaks is higher than that of atoms on submicroscopically smooth surfaces. The same applies to catalytic activity. The most active points of contact substances are submicroscopical edges; peaks and crystal defects. Atoms located at such sites, owing to higher forces acting at these points, can deform adsorbed molecules to a greater extent, and bring them into a state of higher reactivity.

Catalytic activity is influenced also by the order of the surface /for details see Part II, Paragraph C/3/. Surfaces of 1st and 2nd order are easily accessible for gas molecules, and the reaction products obtained are readily diffused from these surfaces, without any hindrance. Surfaces of 3rd order, however, are attained more slowly by the molecules, moreover, the submicroscopical cracks /$\leq$ 1 mμ/ may get blocked up, therefore, these surfaces are less active than those of 1st and 2nd order.

Among contact substances of otherwise identical quality, the highest activity, i.e. the best catalytic effect is found in those of colloidal state /dispersed systems and gels/. The specific surfaces of colloids is relatively the largest, and they possess the highest number of edges and peaks.

3/ Catalyst layers /Catalyst carriers/

In many cases a catalyst can be given a large surface area by transferring the desired material to an inert material of large specific surface area, called "carrier".

Generally it is sufficient to deposit a thin layer of contact substance on the carrier. However, it is essential, that the layer should be of a suitable thickness. A layer of excessive thickness reduces the roughness of the carrier surface. The optimum thickness of layer depends on the quality of catalyst and carrier, as well as on the reaction to be catalysed.

This technique permits to obtain catalytic action with a smaller quantity of material, as the active spots of the catalyst become more easily accessible to the molecules taking part in the reaction.

Another advantage of catalysts on carriers is their improved resistance to high temperatures. The carrier prevents the

recrystallisation of the catalyst layer and retards the decrease in the number of active sites in unit time.

This improved catalytic action of catalysts on carriers is not only due to an increase in specific surface, but, as a rule, also the carrier itself has a certain catalytic effect. This is confirmed by the empirical finding that the catalytic activity of the same catalyst is different when deposited on different carrier substances. The influence of carriers can attain such a high degree that substances originally completely inactive become highly active on the surface of a carrier.

4/ Mixed catalysts

Catalysts consisting of two or more contact substances are called mixed catalysts. The resulting catalytic action of mixed catalysts may be of one of the following kinds:

1. The catalytic action of the components is additive, that is to say each component of the mixture changes /increases or decreases/ proportionally to its concentration the catalytic action.

2. The catalytic action of the mixture is not a resultant of the catalytic action of the components.

a/ The components may increase one another's catalytic action, that is to say, they may mutually activate one another /activating action/;

b/ The components may decrease one another's catalytic action /decreasing action, and its limit case: poisoning action/.

From the practical point of view, activating and poisoning action are of primary importance.

In many cases, activating action /see Part II, Paragraph A/11/ may be of an extent to surpass several times the effect of additivity. In several cases, substances originally inactive, when admixed with a catalyst, may increase substantially the catalytic action of the latter. Substances of this action are called promoters.

Similarly, poisoning effect /see Part II. Paragraph A/11/ may become so pronounced that it completely destroys the high initial catalytic action of the contact substance.

Mixed catalysts are always disperse systems or aggregates /porodine systems/ of mosaic structure. The higher the dispersity of the components the greater the number of the active sites, or, in other words, the higher the activity of the contact substance. The dispersed state of the components also prolongs activity, as the particles of the components prevent each other from becoming coarse through recrystallisation and, consequently, from a diminishing of their specific surface and activity.

In many cases another cause of the high catalytic effect of mixed catalysts is that one of the catalysts adsorbs one of the reactants and the other catalyst the other reactant. For instance, the effect of Ni-Mo or Bi-W catalysts used in the synthesis of ammonia is based on the fact that hydrogen is activated by nickel and nitrogen by molybdenum and tungsten, respectively.

The mosaic structure of mixed catalysts, in which the particles of the component almost contact each other, with only submicroscopical fissures between them, plays an important role. Thus, a particularly strong force field forms between the neighbouring particles, owing to which molecules of the substrate, adsorbed on the grain boundaries, besides being adsorbed to a higher extent, may undergo a deformation, different from that on other parts of the surface.

Thus adsorption taking place along the particle boundaries may shift the reaction in another direction than the individual components of the mixed catalyst. This effect is called synergetical effect. This synergetical effect renders it possible to use mixed catalysts not only for the acceleration of reactions, but also for the changing of their direction /see Part II. Par. A/5/.

The thermal pre-treatment of mixed catalysts is also of great significance. When sintered at low temperatures the components of the mixed catalysts are fused to form defect - like spots. Such defective spots, where each reaction partner undergoes activated adsorption, may be considered as the carriers catalytic characteristics.

5/ Gas and vapour adsorption on solid substances. General survey.

It is well known that porous solid substances as charcoal, silicates, silica gel etc. can accumulate and bind relatively large quantities of gases and vapours. This phenomenon, independently from its cause and from the distribution of the gases or vapours taken up by the solid substance, is generally called "sorption".

Four principal types of sorption are distinguished:

a/ Gases or vapours penetrate into the interior of the solid and on complete permeation form a "solid solution", thus for instance hydrogen in palladium. This is called "adsorption".

b/ Gases or vapours enter into chemical interaction with the solid. This is called "chemosorption" or "chemisorption".

c/ Gases or vapours accumulate on the surface /external and internal/ of the solid, for instance NH_3 on charcoal. This phenomenon is termed as "adsorption".

d/ Gases or vapours condensate in the internal cavities of the solid, thus saturated water vapour in silica gel. This phenomenon is known as "capillary condensation".

Whether the gas or vapour is taken up by the whole mass of the solid or only by its surface, may be established by varying the volume and the mass of the solid independently from each other. If the quantity of gas taken up is independent from the degree of comminution of the solid, the gas has penetrated the whole mass of the solid /"adsorption"/. If, however, the quantity of gas taken up changes with the degree of comminution and is proportional to the surface area, the gas is bound by "adsorption".

Another characteristic is the rate of the gas uptake. Adsorption proceeds at a relatively high rate, whereas the equilibrium of absorption is established rather slowly, in several days, due to the low diffusion rate of gases in solids.

Chemisorption can also be distinguished from adsorption. Adsorption is always a reversible process, whereas chemisorption is generally irreversible. Contrary to adsorption, in chemisorption activation energy is required as a rule.

Here only the most important characteristics of adsorption and capillary condensation will be discussed in detail, as only these two processes play a part in the preparation of products.

6/ Regularities of the adsorption of gases

Strictly speaking, the adsorption of gases on solids is defined as a reversible accumulation of but inert gases, on the surfaces of solids. Inert gases are those which do not enter into chemical interactions with the solid adsorbent and do not get dissolved in it.

Reversibility means that adsorption leads to a true equilibrium called adsorption equilibrium which may be approached from either direction. Adsorption equilibrium means that for identical pairs of substances /identical adsorbent and identical gas as adsorbate/ the quantity of gas adsorbed on the surface of the adsorbent is unequivocally defined by temperature and gas pressure. This means that at constant temperature the quantity of gas adsorbed on the unit surface depends only on the pressure of the gas. On the surface /external and internal/ of the adsorbent the gas molecules form an adsorption layer of definite composition and structure, which is in equilibrium with the neightboughring phases.The two principal characteristics of an adsorption layer are:

1/ its concentration, characterized by the quantity of gas adsorbed, and, 2/ its structure.

A distinction is made between the <u>total</u> and the <u>specific</u> quantity of the adsorbed substance.

The total quantity of adsorbed substance is the excess quantity of gas, expressed in moles or millimoles, contained in the volume of the adsorbate calculated up to the adsorbing surface as compared to the quantity of gas which would be contained in the same volume if it were loaded up to the adsorbing surface with gas at equilibrium concentration.

$$\chi = A - V\varrho \qquad /1/$$

where

a = the entire quantity of the adsorbate
V = the volume of the adsorbate,
ϱ = gas concentration corresponding to adsorption equilibrium.

On dividing the total quantity of gas adsorbed, by the surface area of the adsorbent / Ω / the <u>absolute specific adsorptivity</u> is obtained:

$$w = \frac{x}{\Omega}$$

The quantity of the adsorbed gas related to the unit mass /m/ of the adsorbent is the relative specific adsorptivity:

$$a = \frac{x}{m}$$

The quantity of adsorbed gas may be established either directly, from the increase in weight of the adsorbent, or indirectly, by measuring the decrease of density /or pressure drop/ of the gasous phase. In practice generally the latter method is used.

In the indirect determination of the adsorbed quantity, an adsorbent of known surface or of known mass is brought into contact with a known quantity of gas, in a closed vessel of known volume V. When equilibrium is attained, the gas pressure is measured. From the values thus obtained, isothermic adsorption curve may be plotted, i.e. an adsorption curve giving the adsorbed quantity versus equilibrium pressure at constant temperature.

The same test method is suitable for the determination of the variation of the adsorbed quantity of gas with temperature. This curve, showing the variation of the adsorbed quantity of gas with temperature at constant pressure is the adsorption isobar.

The relationship between the adsorbed quantity/w/and gas pressure or gas density /p/ may be expressed by several equations.

According to the empirical Boedeker-Wilh. Ostwald equation:

$$w = \mathring{\alpha} \cdot p^{\frac{1}{n}}$$

where α = "adsorption value", $\frac{1}{n}$ = "adsorption exponent". The validity of the equation and its applicability to experimental data can be more conveniently examined in the logarithmic form:

$$\log v = \log \alpha + \frac{1}{n} \log p$$

In case of an ideal gas absorption this equation gives a linear relation between the logarithm of the adsorbed quantity and the logarithm of the equilibrium pressure /gas density respectively/. The graphical plotting of this logarithmic correlation permits the determination of the adsorption value /α/, and of the adsorption exponent /$\frac{1}{n}$/. "Adsorption values" usually vary from 0,1 to 1 with the various gases. The value of the adsorption exponent is at low pressures approximately 1, because here the adsorption isotherm is linear and gas is adsorbed according to Henry's equation of adsorption /$v = \alpha.p$/. With increasing pressures $\frac{1}{n}$ gradually decreases and is constant only at medium pressures. Thus, the empirical adsorption equation is valid only at medium pressures. Moreover, according to this equation, the adsorbed quantity will increase continuously with the increase in pressure, while actually the adsorbed quantity is increasing only up to a limit value /saturation/.

Langmuir's adsorption equation may be derived on the basis of molecular-kinetic considerations:

$$v = \frac{v_\infty \cdot p}{p + b}$$

where v_∞ is adsorbed quantity corresponding to a saturated monomolecular layer, and

b is quality constant of the a substance.

According to this assumption, an ideal gas adsorption results at the most in the formation of a monomolecular adsorption layer. However, adsorbed molecules carry out a certain degree

of movement in the adsorption layer along the adsorbing surface. Thus, the adsorption layer behaves as a two-dimensional gas.

As a further development of the conception of Langmuir, Brunauer, Emmett and Teller established the following isotherm for polymolecular adsorption layers /BET isotherm/:

$$a = \frac{a_\infty \cdot C \cdot p}{/p_o - p/\left[1 + /c-1/\frac{p}{p_o}\right]}$$

where p_o is the saturated vapour pressure, and C is a constant characteristic of the given system.

Physical sense of the constant C:

$$C = e^{/E_1 - E_2/ /RT}$$

where E_1 is the adsorption energy of the first layer and E_2 is the adsorption energy of the following layers, the latter being approximately equal with the heat of condensation of the adsorbate.

On a thermodynamical basis Harkins and Jura have derived the following equation:

$$\ell n\ p/p_o = D - \frac{C}{a^2}$$

where p/p_o is the relative vapour pressure, a is the relative specific adsorbtivity, and D and C are constants, having the following meaning:

$$D = \ell n \frac{p_1}{p_o} + \frac{b\,\Omega^2}{2RTa2_1}$$

$$C = \frac{b \cdot \Omega^2}{2\ RT}$$

where p_1 is the vapour pressure at which the adsorption layer just condenses, and a_1 is the adsorbed quantity in

mol/g belonging to p_1. This equation is in a fair accordance with experimental data of a relatively high pressure range.

The influence of temperature on gas adsorption is usually significant. Under otherwise identical conditions, the quantity of adsorbed gas decreases with the increase of temperature.

According to Freundlich, the dependence of adsorption on temperature at constant pressure is given by the following empirical equation:

$$\log x_t = \log x_0 - k_1 - k_2 \log p/t,$$

where x_t is the quantity adsorbed at the temperature t, and x_0 the quantity adsorbed at 0° C, p is the pressure, and k_1 and k_2 are constants independent from pressure and temperature.

7/ Effect of the quality of gas on adsorption

Every gas is adsorbed more or less on the surface of every solid substance. Under otherwise identical conditions /i.e. at identical temperature and pressure/, the same adsorbent generally will adsorb greater quantities of the gas of higher boiling point, and, in case of identical boiling points, of the gas having a higher molecular weight.

From gas mixtures every component is adsorbed to a smaller or greater extent, the adsorption layer is, therefore, in such cases a mixed layer.

A gas already adsorbed may be replaced on the adsorbent surface by any other gas having a higher adsorptivity under the given conditions than that originally adsorbed.

Differences in the adsorption of the single components of gas mixtures may be of such extent that the components can be almost completely separated on this basis /gas chromatography/. This selective adsorption is particularly very pronounced with gas mixtures containing on one hand components difficult to condense and on the other hand a readily condensing component.

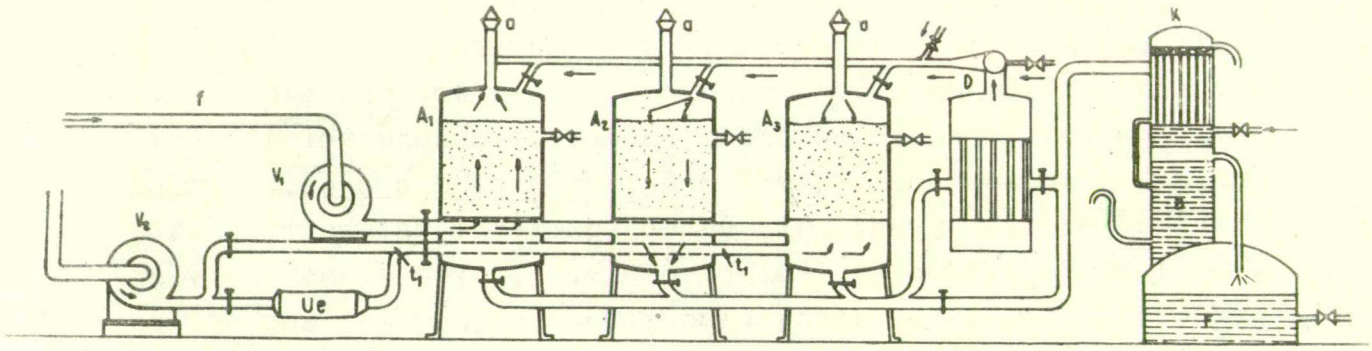


Figure 16

Adsorption battery according to Bayer for the recovery of vapours of solvents

8/ The recovery of vapours of highly volatile liquids

The process includes three main steps. In the first step, the vapour mixture is passed over the adsorbent, and the vapours are fixed by the adsorbent; in the second step the adsorbed compound is desorbed from the adsorbent by indirect heating or by direct introduction of steam; finally, in the

third step the adsorbent is regenerated, i.e. reactivated. Regeneration is attained by drying, that is to say, by heating to the required temperature and cooling. For this purpose, active carbon, silica gel and active alumina are used as adsorbents.

Figure 16 shows an adsorption plant of continuous operation, consisting of three adsorbers /A_1, A_2, A_3/, a boiler /D/, a condenser /K/ and a separator /B/. Valve V_1 sucks in the gas or air containing the vapour to be recovered and forces it upwards through adsorber A_1 packed with active carbon. The gas or air free of vapour leaves through the chimney. Through adsorber A_2, containing an adsorbent saturated with the vapour, superheated steam is passed downwards to displace the adsorbed vapours. The mixture of steam and vapour passes into cooler K where vapours are condense and the condensed mixture is collected in separator B. Simultaneously, in the third adsorber, A_3, the carbon already freed of the adsorbed vapours is dried and cooled, that is to say, regenerated. For this purpose first hot, then cold air is blown upwards through the carbon layer with the air pump V_2. When the carbon layer has cooled to room temperature, it can be used again for the adsorption of vapours.

In industrial practice the following terms are frequently used:

Loading of adsorbate: the quantity adsorbed by 100 g adsorbent, usually expressed in per cent by weight.

Equilibrium loading: the loading of adsorbate at adsorption equilibrium.

Saturation loading: the adsorbed loading, i.e. the quantity, corresponding to adsorption equilibrium in a saturated mixture of vapour and air.

Additional loading: the quantity of adsorbed steam of vapour that can be removed from the adsorber.

Residual loading: the quantity of adsorbate that cannot be removed from the adsorber.

Retentivity: The binding power of the adsorber which retains the residual loading. Carbon of high retentivity, for instance, is unsuitable for the recovery of solvent vapours, on the other hand, it is suitable for the loading of gas mask filters.

Breakthrough: the moment when the first traces of the adsorbate appear in the gas /or air/ passing through the adsorbent layer, i.e. when adsorption begins to be imperfect.

9/ Capillary condensation

Distinction is made between two main cases: a/ the condensed vapour does not wet the adsorbent and b/ the condensed vapour is wetting the adsorbent.

a/ The adsorption of vapours of not wetting liquids occurs in the same way as that of gases above critical temperature. The process is governed by the same laws as the adsorption of gases.

b/ The adsorption of vapours of liquids wetting the adsorbent is substantially different.

Below the critical temperature vapours of liquids wetting the adsorbent are according to an isotherm with an inflexion point. With the increase in pressure, the adsorbed quantity first increases according to the curve representing the normal isotherm, but in the vicinity of saturation pressure, it suddenly increases at a higher rate. Owing to this, at

higher pressures the isotherm assumes a concave shape and at saturation pressure it forms a vertical line /see Fig.17/.

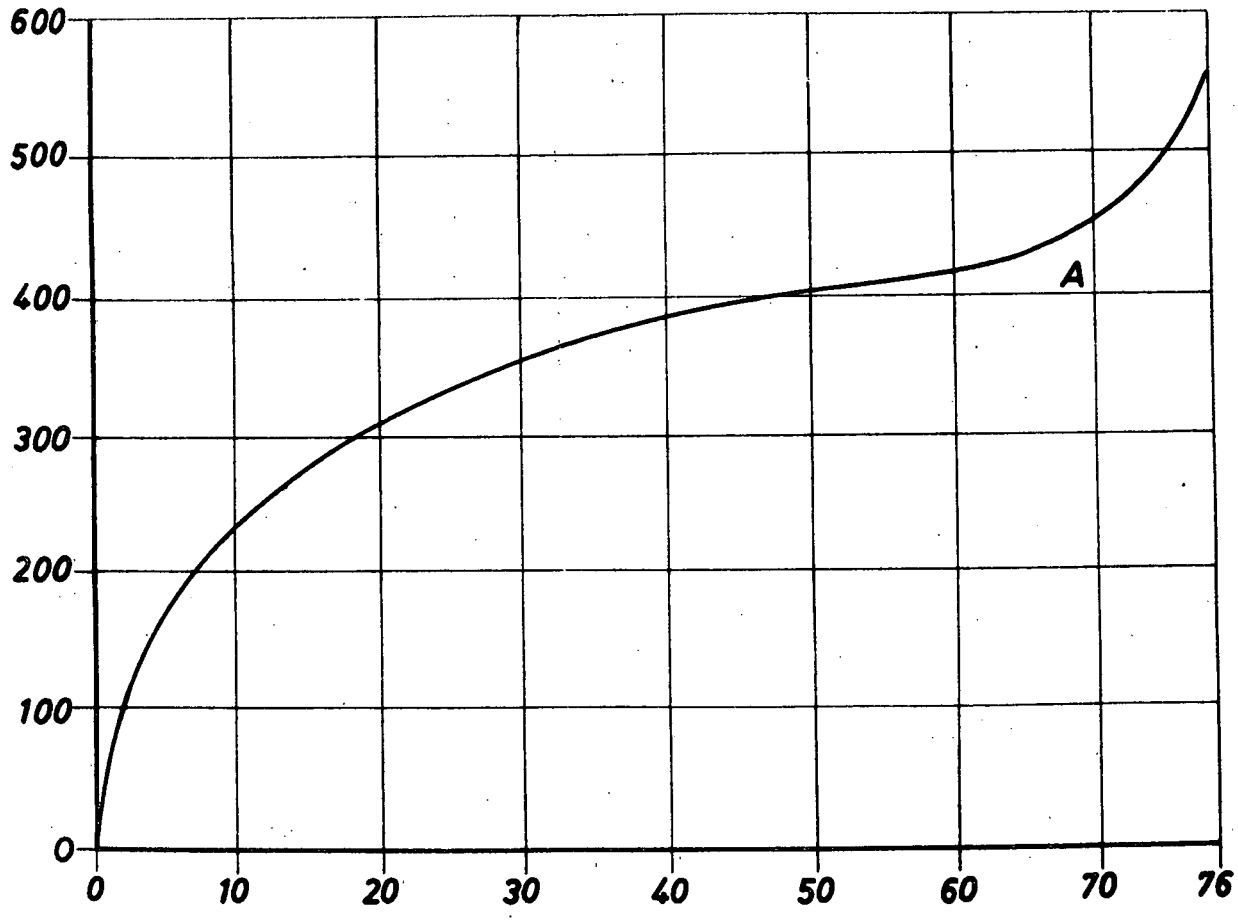


Figure 17
Adsorption isotherm of a liquid wetting the adsorbent

The specific shape of the vapour adsorption isotherm is due to condensation by capillary forces to capillary condensation.

It is well known that the pressure of saturated vapours of a wetting liquid is lower in capillaries than that of its saturated vapour over a plane liquid surface. According to Thomson, the decrease in tension may be calculated by the following equation:

$$\ln \frac{p}{p_r} = \frac{2\sigma}{r} = \frac{M}{RT\varrho} ,$$

where p_r is the pressure of the saturated vapour of the liquid in the capillary, p the pressure of the saturated vapour of the liquid over a plane surface, σ the surface tension of the liquid, M the molecular weight of the liquid, r the radius of curvature of the liquid in the capillary, R the universal gas constant, T the absolute temperature, and ϱ the density of the liquid.

If an adsorbent having capillaries of various dimensions comes into contact with the vapour of some wetting liquid, first, at low pressures, even on the surfaces of the smallest capillaries a simple adsorption takes place and only an adsorbed molecular layer is formed. If the adsorbent contains only extremely small, amicroscopical capillaries / $\leqq$ 1 mμ/, at the most a monomolecular adsorption layer will be formed and no condensation occurs. If, however, the adsorbent contains larger amicroscopical, for instance, submicroscopical /1 mμ - 500 mμ/ capillaries, or narrowing, wedge-shaped cracks, at adequately higher pressures liquid will condense in the submicroscopical capillaries and voids. The narrower the capillary or crack, the lower the vapour pressure in equilibrium with the liquid. Vapour penetrating the voids will condense until the tension of the liquid condensed in the adsorbent becomes equal to the pressure of the external vapour. The higher the pressure of the saturated steam, the wider capillaries will be filled with condensate.

It follows from the equation of Thomlison that a liquid surface of a determined radius of curvature r, being in equi-

librium with the vapour, belongs to each value of vapour pressure p. Thus, at each vapour pressure p, all capillaries, the radii of which are smaller than the value calculated from the Thomlison equation, will be filled with liquid. With the increase of vapour pressure, the width of the capillaries filling up with liquid will increase. If all the capillaries of the adsorbent were of the same size, capillary condensation would take place at a single given vapour pressure. In this case the isotherm would present a point of discontinuity at this pressure. However, since the adsorbents always contain capillaries of very different sizes, the isotherm, from the p value on where capillary condensation begins, will steeply rise until complete condensation.

In practice in the adsorption of vapours - for instance on active carbon or silica gel - quantitatively the most important role is played by capillary condensation. Actually, the quantity of vapour bound by an adsorbent by "adsorption" proper is relatively small. Thus, as regards the activity of adsorbents used for vapour adsorption, the structure of the adsorbent and the size of its capillaries are of primary importance. Capillaries and internal cavities of either too small /amicroscopical/ or too large cross section /larger than submicroscopical/ are unsuitable for capillary condensation. The wettability of an adsorbent is also of great importance. This becomes evident, under others, from the fact, that active carbon as a hydrophobic substance, is a very good adsorbent for vapour of organic compounds, but is unsuitable for the adsorption of water vapour. On the other hand, for instance, highly porous silica gel being hydrophilic, vigorously adsorbs water vapour, while vapours of organic compounds will be adsorbed only in dependence of their wettability. Acetone vapours, for instance, are readily adsorbed by silica gel, but benzene vapours only to a very slight degree.

10/ Adsorption hysteresis

In connection with the adsorption of vapours it has often been experienced that desorption is not the simple inversion of adsorption. In the desorption isotherm a higher rate of adsorption corresponds to the same equilibrium pressure than that in the adsorption isotherm. This phenomenon is denoted as adsorption hysteresis. Figure 18. shows the adsorption isotherms of benzene, alcohol and water vapour. In all three cases, dry silica gel is the adsorbent. Up to point O_1 the vapours undergo simple adsorption; along the section OO_1 of the isotherm adsorption is fully reversible, that is to say, the quantity of adsorbed vapour is independent of the direction of the change /increase or decrease/ in pressure. Between points O_1 and O_2, however, the process becomes irreversible in the sense that the quantity of adsorbed vapour is found to be higher, if starting from the saturation point vapour pressure is reduced, than when starting from a lower vapour pressure and going upwards along the isotherm.

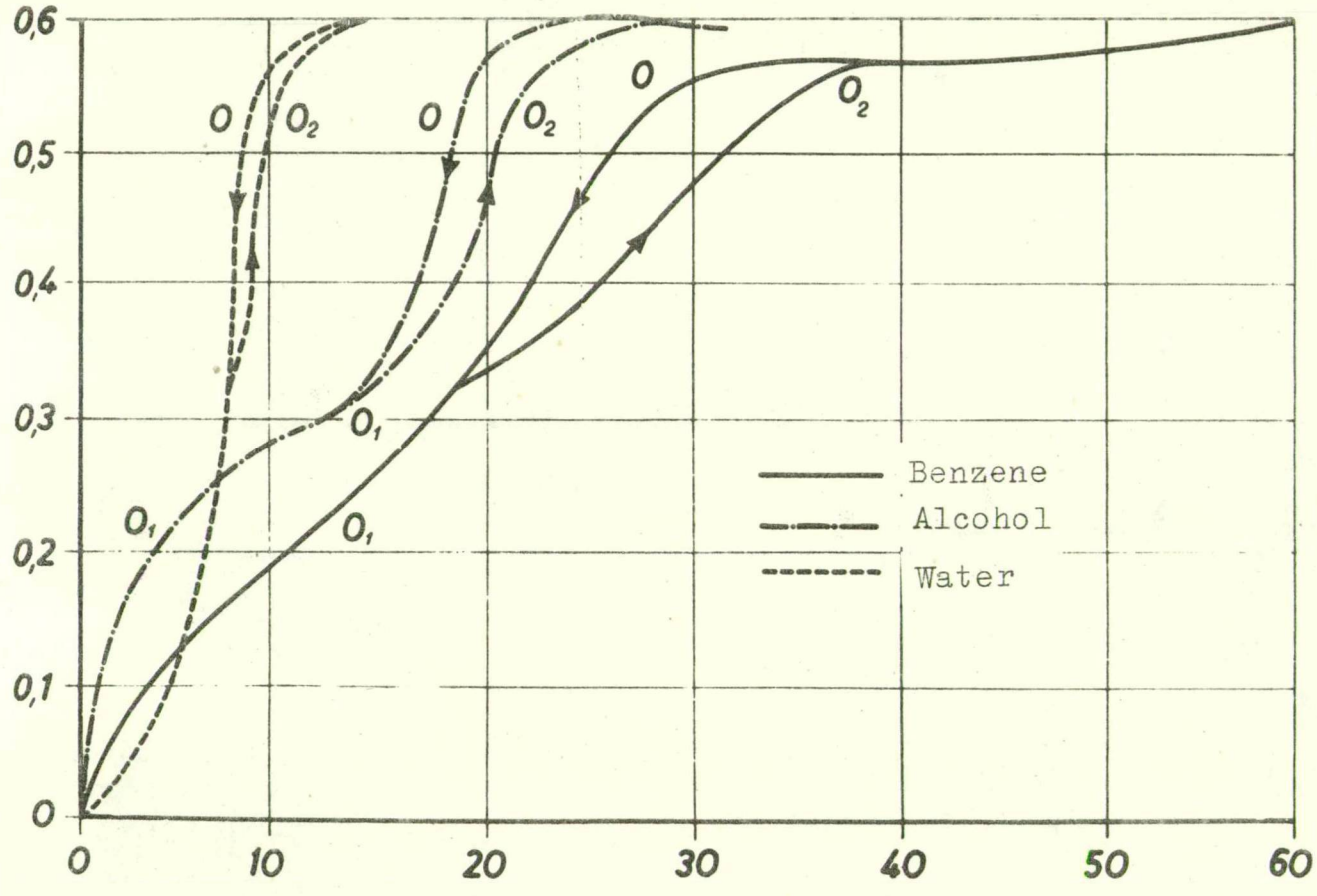
Generally, the principal cause of adsorption hysteresis is imperfect wetting owing to the adsorption of air. As long as vapour does not condense in the capillaries of the adsorbent, the adsorption of the vapour is reversible. At the pressure corresponding to point O_1 capillary condensation begins, and liquid accumulates in the capillaries. If the adsorbent had adsorbed air, its wettability is lower than in the case when it is completely free of air. Therefore, when proceeding towards higher pressures along the isotherm, the adsorbent will bind less vapour at a given pressure than the amount which would be condensed in case of complete wetting. After a certain time the condensate displaces the adsorbed air and the walls of the capillaries become wetted. Therefore, when the pressure is reduced, equilibrium is established between the liquid contained in capillaries with already completely wetted walls and the vapour in the external space. As surfaces

in such capillaries have smaller radii of curvature, and consequently a lower tension, more liquid will be retained in the adsorbent, than in the case of an increase of pressure.

The correctness of this interpretation is supported by the experimental fact that adsorption hysteresis is generally absent in the case of adsorbents from which air has been previously completely removed /e.g. by ignition/. Hysteresis manifested in the case of heat treated adsorbents is to be attributed to the presence of capillaries of irregular form, the so called "ink bottle" capillaries, which widen inside.

Adsorption hysteresis and its originator: displacement adsorption are also of great practical significance, and cause, in many instances, disturbances. For instance, when recovering organic solvent vapours from air, the adsorption of atmospheric humidity may influence disadvantageously the process, inasmuch that vapours already adsorbed might be displaced from the adsorbent /for instance, silica gel/ by water vapour.

Saturation pressure of H_2O | Saturation pressure of C_2H_5OH | Saturation pressure C_6H_6



Steam pressure in mm Hg

Figure 18

Adsorption isotherms of benzene, alcohol, and water vapour

C/ EFFECT OF THE ADSORBENT ON GAS ADSORPTION

1. Determination of the surface of the adsorbent

The adsorptivity of various adsorbents can be precisely expressed and compared by the absolute specific absorption. Adsorptivity characterized by the absolute specific adsorption depends exclusively on the surface properties of the adsorbent. Absolute specific adsorption, however, may be determined only if the actual surface area of the adsorbent is known.

For the determination of the surface of adsorbents methods based on the following principles are used:

a/ If the adsorbent has only an external surface, any method suitable for the determination of the dimensions and of the form of the adsorbent can be used. /Microscopic, ultramicroscopic, electronmicroscopic methods and all those indirect methods, lending themselves to the determination of the dispersivity of disperse systems consisting of compact particles./

When determining the surface area of an adsorbent having a disperse structure composed of particles of different size, the distribution curve of the particles must be determined. The curve can be plotted by taking photomicrograms of the particles spread on a glass plate and measuring the surface of the projection /projection surfaces/ of a fairly large number of particles. The surface of the projection is equal to a quarter of the total surface area. When the mass of the particles is known, the surface area of 1 g of the adsorbent can be calculated.

The roughness of the surface is neglected in this method. However, with methods of higher sensitivity, extremely fine grooves, cracks, and irregularities can be detected even on

surfaces of apparently perfect smoothness. This unevenness represents structural elements playing an important role in adsorption processes. Therefore, it is to be expected that the surface area determined by the geometrical method described above is significantly smaller than the actual surface.

b/ One of the methods for the determination of the surface area of <u>porous adsorbents</u> is based on the experimental measurement of the volume of the internal, voids and capillaries, and the linear dimensions of their cross sections. The ratio of surface to volume is 3/r for spheres /r = the radius of the sphere/, 2/r for cylinders and 6/l for cubes /l = the length of the edge of the cube/. Capillaries of various shapes can be averaged by using the concept of the equivalent radius. The equivalent radius is the radius of that capillary of circular cross section, the cross sectional area of which is equal to the average cross sectional area /q/ of all the capillaries, that is:

$$r_a = \sqrt{\frac{a}{\pi}}$$

Thus the ratio of surface to volume for a sphere is: $\frac{3}{r_a}$, for a cylinder: $\frac{2}{r_a}$, for a cube: $\frac{3,4}{r_a}$, for a square-base column: $\frac{2,3}{r_a}$.

The mean value of the coefficients is 2,7. Thus, the surface of 1 g of material is

$$O = \frac{2,7 . V_q}{r_a \cdot q}$$

where V_q is the total volume of voids and capillaries in an adsorbent of the quantity q. If V_v of the volume of the internal voids present in 1 cm^3 of the adsorbent, the specific surface is given by the following formula:

$$\Omega = \frac{2,7 . V_v}{r_a}$$

According to this, the internal surface may be determined by any of the methods suitable for the measurement of the total volume of the internal voids, i.e. of porosity. These methods are: microscopic determination of the pore size, measurement of capillary condensation, capillary pressure /bubble pressure/, diffusion rate and fluid permeability.

The accuracy of surface determination based on the measurements of the volume of the internal voids is satisfactory only if the internal surface is not too coarse, because the roughness of the surface has not been considered in the determination of the value of the coefficient /2,7/ mentioned above. Accordingly, methods have to be supplemented or checked by other techniques in order to furnish reliable experimental data regarding the surface of adsorbents.

2. Surface determination by adsorption methods

a/ Relative method: It consists in the comparison under identical conditions of the adsorptivity of an adsorbent of unknown surface with the adsorptivity of an adsorbent of known surface having the same quality and surface characteristic.

b/ Absolute method: when the maximum quantity which can be adsorbed by 1 cm^3 is known, the surface area may be calculated from the adsorbed quantity at saturation.

a/ In the relative method the maximum quantity that may be adsorbed is measured under identical test conditions /identical adsorbate, identical temperature/, on a plate of the same quality characteristics as those of the adsorbent but of known surface, and on a weighed quantity of the adsorbent to be tested. The surface then may be calculated by the following simple relationship:

$$\frac{\text{surface of the adsorbent}}{\text{surface of the plate}} = \frac{\text{quantity adsorbed by the adsorbent}}{\text{quantity adsorbed by the plate}}$$

b/ The absolute method has several variants. Conditions are relatively simple, when the maximum adsorption corresponds to a monomolecular or a monoatomic layer. In this case, the number of the "adsorption centres" on the surface, and, in some cases, the number of surface atoms capable of adsorption /z/ can be determined.

Adsorption centres are surface elements capable of adsorption.

Assuming that the adsorption layer formed is at the maximum /at saturation/ monomolecular, the surface of 1 g of adsorbent is:

$$O = z \cdot \omega_M$$

where ω_M is the fraction of surface per one molecule.

Assuming that in a saturated adsorption layer the molecules are as closely packed as possible, the part of the surface occupied by each molecule will be a regular hexagon and the radius of the circle to be drawn in this hexagon is equal to the radius of the spherical molecule /or atom/. The surface of the hexagon is:

$$\omega_M = 3{,}43 \cdot p_M^2 = 1{,}33 \left(\frac{V_{mol}}{N} \right)^{\frac{2}{3}} cm^2$$

The number of adsorption centres may be determined from the adsorbed quantities corresponding to the closely packed monomolecular adsorption layer. Evidently:

$$Z = a_\infty \cdot N \qquad /N = \text{Avogadro-number}/$$

The value of a_∞ is determined from one of the kinetic isotherms, generally from the BET-equation.

The specific surface can be calculated from the Harkins-Jura equation by the determination of the constant C, since the following relation exists between this constant and the specific surface: $\Omega = \sqrt{\frac{2RT}{b}} \cdot C = kC$

According to Harkins and Jura, the constant k is independent of the quality of the adsorbent and depends only on the quality of the adsorbate. If, therefore, the value of the constant k is determined on standard adsorbents /of known surface/ for different adsorbates, the specific surface can be directly calculated when C is known.

For the determination of the surface of adsorbent the most reliable methods today are the adsorption methods. When the surface of the adsorbent cannot be determined, the only method for the estimation of adsorptivity is based on the relative specific adsorption, i.e. the quantity adsorbed by 1 g of the adsorbent.

In the evaluation of industrial adsorbents, the relative specific adsorption is of great practical importance, being the most direct measure of the "activity" and, thus of the economic use of adsorbents.

Relative specific adsorption, /a/ depends on the following factors:

a/ Specific surface of the adsorbent;
b/ Morphological properties of adsorbent: dimensions, form and radius of curvature of the surface of the capillary system and the voids; dimensions, form and spatial distribution of particles in the case of disperse adsorbents.

c/ Amicroscopical and submicroscopical structure of the surface of the adsorbent, crystalline of amorphous character, amicroscopical and submicroscopical roughness;

d/ Properties of the adsorbent following from its chemical composition; chemical affinity to the adsorbate, polar or apolar character.

3. Morphological properties of adsorbents

There exists a close correlation between the specific surface and the morphological properties of an adsorbent. Among adsorbents colloidal systems have the highest activity, provided, of course, that they meet other requirements in respect to adsorptivity, to be discussed in the following. Gas adsorbents used in chemical industry may be classified into two main types.

a/ Disperse systems or their agglomerates /porodine systems/, for instance, metal powders.

b/ Gels of porodine structure and their powders, such as various carbon preparations, metal oxide gels, silicates etc.

Solids of macroscopical dimensions, having only external surfaces, e.g. metals, are of less importance as "adsorbents", and are used only in special cases.

The problem, whether the difference in the adsorption activity of two adsorbents is due only to the difference in their specific surfaces /dispersity of degree of deformation/ or also to differences in some other characteristics, may be decided on the basis of the adsorption isotherms. If the adsorbents differ only in their specific surface areas, but their adsorptivity per unit surface is the same, they give under otherwise identical conditions so-called affin adsorption isotherms, i.e. in the empirical adsorption equation

$$a = \alpha\, p^{1/n},$$

referred to the same adsorbate, only the adsorption value /α/ is different, while the adsorption exponent /1/n/ is identical. The relation between the values is the same as that between the specific surface areas. Thus, the relative specific surface areas of the adsorbents can be determined from affin adsorption isotherms.

In the case of adsorbents with internal surface, it is reasonable to differentiate three orders of surfaces:

Surface of 1st order: the external surface, and the surfaces of cavities, voids, and channels of coarse /macroscopical and microscopical/ dimensions;

Surface of 2nd order: the surfaces of submicroscopical /1mμ-500 mμ/ voids, channels, and capillaries;

Surface of 3rd order: the surfaces of amicroscopical / ≦ 1mμ/ voids and channels.

This differentiation is justified as the surfaces of different order behave substantially differently in the course of adsorption. On surfaces of the 1st order, polymolecular adsorption layers may develop without any hindrance, because of the wideness of the cavities. However, on surfaces of the 2nd and 3rd orders, provided the adsorbent is completely rigid, only correspondingly thinner adsorption layers may be formed, and thus, the quantity absorbed will be less. Surfaces of the 3rd order permit only the formation of monomolecular adsorption layers, as only small molecules penetrate into the channels of amicroscopical dimensions.

The difference in the order of the surface causes particularly great differences in capillary condensation. Mainly surfaces of 2nd order are active from the point of view of capillary condensation. The radius of curvature of liquid surfaces contained in the coarser voids is not small enough to cause a practically significant difference between the tension of the liquid on the surface of 1st order and the vapour pressure of liquid of plane surface. Therefore, surface of the 1st order are of secondary importance from the point of view of capillary condensation. As in amicroscopical interstices, only monomolecular adsorption layers are formed,

there is no capillary condensation. According to this, only colloidal absorbents, e.g. gels are suitable for capillary condensation.

In the case of pulverized adsorbents, the compactness of the aggregate may play an essential role in adsorption and particularly in capillary condensation. In monomolecular adsorption, the compactness of the aggregated particles does not affect significantly the adsorptivity. However, in polymolecular adsorption, and particularly in capillary condensation, the compactness may have a very considerable effect. Too loose or too compact aggregates are equally unfavourable in capillary condensation, because both contain but few submicroscopical voids. In the compactness of an aggregate the size, the size distribution and the form of the particles play a decisive role.

The structure of the adsorbent surface is one of the most important physical factors determining the activity of adsorbents. Compared to submicroscopical and amicroscopical unevenness, "roughness", often all other otherwise significant factors play only a subordinate role. In many instances the "activation" of adsorbents is based on increasing the submicroscopical and amicroscopical roughness of the surfaces by heat treatment, chemical etching or leaching, "forming" hereby the surface.

The structure of the surface, excepting those cases, where the adsorbent is subjected to an after-treatment, is generally determined by the internal structure of the adsorbent, by its crystalline or amorphous character. The surface of a crystalline adsorbent is usually less rough than that of amorphous adsorbents. This fact explains the experimental finding that the adsorptivity of amorphous adsorbents is higher than that of crystalline adsorbents.

4. Influence of the chemical composition of the adsorbent on adsorption

The influence of the chemical composition of the adsorbent on the adsorption of various gases is not specific. Various gases are usually adsorbed on various adsorbents in the same sequence and nearly in the same ratio, provided there is no chemical interaction between adsorbent and adsorbate. For example, the sequence of adsorption of the following gases $H_2 < O_2 < N_2 < H_2S < NH_3$ is equally valid for carbon, asbestos, pumice and silica gel adsorbents. From this follows that for the experimental comparison of the adsorptivity of various adsorbents it is generally sufficient to plot the adsorption isotherms for a single gas.

5. Methods for the testing of adsorbents

The testing of adsorbents involves the determination of three principal groups of characteristics:

a/ chemical composition,
b/ physical properties,
c/ adsorptivity.

a/ As regards chemical composition, emphasis is laid not on the basic material of the adsorbent, but on the quantity and quality of "foreign" substances. Distinction is made between volatile and non-volatile foreign substances. For gas adsorbents volatile substances, such as: water and various adsorbed or unstable substances are of decisive importance. These substances can greatly influence the reactivation of the adsorbent. The quality and solubility of non-volatile components is of particularly great importance in the adsorption of vapours, because they may get into the condensed vapours and constitute detrimental contaminations.

b/ The testing of physical properties includes in the case of adsorbents of disperse structure the determination of the dispersivity, the form of particles, of the internal structure and volume weight; in case of porous adsorbents the determination of the microscopical structure and of the porosity and in both cases the determination of the specific surface and of strength.

In the case of adsorbents of disperse structure, in general already a microscopic investigation gives information on the size and form of the particles and on technical history of the adsorbent. Microscopic examinations may be complemented by other methods, suitable for the determination of dispersivity, thus by the sedimentation method, etc. Microscopic examination furnishes valuable data also regarding porous adsorbents, particularly if the test is carried out on suitably prepared sections. Electron microscopic examination gives information on the submicroscopical structure and X-ray spectrography on the crystal structure.

The volume weight of adsorbents is of practical importance in the designing of adsorbers, where it is necessary to know the space to be occupied by the adsorbent in the gas space.

Strength characteristics, particularly the compression strength and abrasion resistance are also important physical properties in the practical application of adsorbents. Adsorbents of poor strength are pulverulent, and this influences their volume weight and their compactness. Due to this, these are less suitable for industrial purposes than adsorbents of high strength.

c/ Adsorptivity is evaluated on the basis of adsorption isotherms. In simple cases it is sufficient to determine three points of the isotherm; it is, however, always recommended to carry out the test with the same gas for the adsorption

of which the adsorbent is intended. If the adsorbent is to be applied for selective adsorption, for instance, for the recovery of solvent vapours from air, it is of particular importance that the test should be carried out with the given industrial gas or gas mixture. In such cases also equilibrium loading, residual loading, retentivity and breakthrough are to be determined. In some cases the determination of the adsorption rate is also of importance. In practice, adsorption rate is defined as the volume of gas which, at a specified constant flow rate, is adsorbed in unit time by a specified layer of the adsorbent.

6. Gas adsorbents containing active carbon

Adsorbents containing carbon gained a general industrial importance at the beginning of the present century. The first techniques developed in this period resulted in the production of carbon-base adsorbents of far better efficiency than charcoal, bone black and similar carbon products. Carbon base adsorbents of high adsorptivity produced by these new processes have been brought in circulation under the name of "active carbons".

All active carbons are characterized by high porosity and consequently by a large specific surface area. As regards chemical composition, none of the active carbons is pure carbon. All of them contain more or less oxygen and hydrogen, which may be residues from the activation process. Active carbons always contain inorganic ash components. All these accessory constituents, however, play only a subordinate role in activation as compared to the specific surface, pore system and surface structure. Investigations in this field have proved that adsorptivity is a property of pure carbon. When the carbon particles are smaller than 0,001 mm, the adsorptivity increases rapidly with the degree of dispersion. Other experimental results showed that needle-form carbon particles have a higher adsorptivity than lamellar particles. Active

carbons of high activity are formed by clusters of submicroscopical crystal needles.

Active carbons are essentially produced by the carbonisation of a carbon-containing material, for instance wood, and by heating the obtained "coke" for a longer period at an adequate temperature in the presence of some activating agent. This process, called activation, serves to improve the adsorptivity.

In large scale industrial production a great variety of raw materials are used, such as wood, peat, charcoal, lignite, lignite coke, husks of stone-fruits /cocoanut, hazelnut, almond/, animal and vegetable wastes, rubber wastes, algae, residues of cellulose production, wastes of petroleum refining, etc.

Activating agents may be gases, liquids or solids. Gaseous activating agents are: water vapour, air and carbon dioxide. A liquid activating agent is, for instance, phosphoric acid. Solid activating agents are zinc chloride, potassium carbonate, alkali- and alkali earth metal thiocyanates, potassium sulphide, potassium sulphate. In practice, generally a distinction is made between "gas-activated" and "chemically activated" carbons.

a/ In activation with gas, the starting material is a substance previously carbonized, thus charcoal, coal of fruit stones or coke. These "primary coals"may be considered as adsorbates containing carbon, hydrocarbons, and other compounds of high carbon content /tar/. The adsorptivity of these substances is low and they become active only on removing the adsorbed hydrocarbons and other tar-like products. The activation process must be directed in such a way that adsorbed substances shall oxidize quickly, while pure carbon only slowly. Air between 350 and 450°C or steam or a mixt-

ure of steam and carbon dioxide of a temperature from 800 to 1000°C are used as oxidizing gases.

By passing a larger amount of steam through the carbon, the activity of the product becomes higher, but the yield will be poorer. In order to produce granulated active carbon, primary carbons are pulverized prior to activation and then pressed into pellets.This process is used for the production of active carbons type "Norit". Pulverized carbons can be activated also in a fluidized state. This permits activation to proceed on a larger surface and results in carbons of higher porosity, lower volume weight and higher activity.

b/ Among chemical activation techniques, the most widely used is the zinc chloride process. Primary coal /charcoal, peat, coal of fruit stones is first carefully cleaned, usually with acids, and then saturated with a zinc chloride solution, or admixed with zinc chloride solution to form a thick pulp.The pulp is dried at a slowly rising temperature, then heated to 400 to 800°C. Zinc chloride, being a strong dehydrating agent, removes hydrogen and oxygen from the non-carbonised parts in the form of water, carbonizing simultaneously these incompletely carbonized constituents. This results in a carbon or carbon skeleton of a very fine distribution. After heat treatment, the carbon is leached several times, and if necessary, ground and dried. Active carbons called "Carboraffin" are produced by this method.

In many cases, chemical activation may also be combined with activation by water vapour.

Chemically activated carbons are characterized by a higher or lower ash content, usually a residue of the activating agent. This relatively minute ash content is also of importance in the adsorption process because it renders the surface of the carbon polar.

Irrespective of the method of their preparation, active carbons produced industrially are classified into three groups in respect to their field of application:

a/ gas adsorption carbons /A carbons/
b/ decolourizing carbons /E carbons/
c/ medicinal carbons /M carbons/.

Gas adsorption carbons are granulated, but decolourizing and medicinal carbons are very fine, pulverized preparations, their particle size being smaller than 0,01 mm.

This classification is justified because of the differences in the adsorptive capacity of different active carbons. Gas adsorption carbon of high activity, while eminently suitable for the adsorption of gases, is generally a poor adsorbent of solutes, even when pulverized. Similarly, efficient decolourizing carbons are not always suitable for use as gas adsorbents. These differences may be ascribed besides differences in physical structural properties to the presence of "foreign" substances, to ash constituents. Adsorption test is indispensable when evaluating an active carbon.

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D. APPLICATION OF PYROPHOROUS METAL PREPARATIONS IN CATALYSIS

Introduction

Pyrophorous properties, mainly of metals, were discovered in the beginning of the last century. Certain non-precious metals and metal oxides when produced under particular conditions are highly reactive. These substances on coming into contact with atmospheric oxygen, take fire spontaneously and, under intensive glowing, burn to form metal oxides of high oxidation state. The word pyrophorous itself originates from the Greek pyr = fire and phoros = carrier.

Substances of such behaviour are called spontaneously pyrophorous. Spontaneously pyrophorous substances may be converted into a latent pyrophorous form /see Part II. Paragraph D/4/, or they may be produced in this latent form if the basic materials and the conditions of production are selected adequately. Latent pyrophorous materials can be kept in open air, without self-ignition, however, when brought into contact with a hot object /a hot wire or a glowing stick/ a local ignition occurs and the whole mass of the preparation begins to glow almost instantaneously.

Generally speaking all metal preparations having considerably lower ignition temperatures than common metals are considered as pyrophorous.

No definite criterion of the pyrophorous nature is known. Attempts have been made to consider that concentration of oxygen as the quantitative criterion of pyrophorous nature, which destroys the pyrophorous properties at a specified temperature and in a given time. It was also attempted to establish correlations between pyrophorous nature on the one

hand and dispersion grade, catalytic activity and adsorptivity on the other hand. However, all these methods of evaluation greatly depend besides the quality of the metal on the initial materials used for the preparation and on other parameters, and are, therefore, unsuitable for the quantitative characterization of pyrophorous properties.

Pyrophorous behaviour is the manifestation of the extremely reactive form of certain metals and some metal oxides of low oxidation state, showing a parallelism with the catalytic, adsorptive and other properties of these substances.

Pyrophorous behaviour has been observed with a number of non-precious metals such as Fe, Co, Ni, Cu, Zn, Pb, Cd, In, Sn, Ti, Zr, As, Sb, Bi, V, Cr, Mo, W, U, Mn. Presumably Al, Ge, Hf, Nb, Ta, Mo, Re can also be produced in a pyrophorous form. Pyrophorous FeO, MoO_2, UO_2, Cr_2O_3 /on carriers/ etc. are well known.

1. Production of pyrophorous metal preparations
   The influence of the conditions of production on the degree of activity

In the following a short description will be given of the most typical methods of production of pyrophorous metal preparations, supplemented in some of the cases with the description of the production of the initial materials.

a/ Reduction of metal compounds in hydrogen. This method is used primarily for the production of pyrophorous metals from metal oxides and from metal hydroxides. The optimum temperature of reduction varies from metal to metal, depending on the nature of the anion and on the activity of the compound to be reduced. The possible presence of analogous metal compounds also influences the course of the reduction. Generally, higher temperatures can be applied for preparations on carriers than for those without

carriers. The following table gives the temperatures at which complete reduction is still to be obtained /these temperatures, however, cannot be considered as thermodynamically well-defined/.

Metal	Fe	Co	Ni	Cu	Mo	W	Bi
Temperature, °C	350	300	150	100	550	700	170

The temperature of the reduction may determine besides the activity of the preparation also the type of its crystal structure. For cobalt/III/hydroxide the following conditions prevail:

Temperature of reduction, °C	300	400	500	600	700	800
Crystal structure	Co /hexagonal/			Co cubic		
Pyrophorous character	Spontaneously pyrophorous		latent pyrophorous	not pyrophorous		

When oxides are used as starting materials the preparation is to be expected to contain small amounts of oxides. Besides oxides and hydroxides also carbonates, formates, oxalates etc. are frequently used as starting materials. With the latter - particularly at low temperatures - the pyrophorous preparation may contain residual carbon as contamination. Anions of high space requirement reduce the density of the produced metal and result in a high activity.

Pyrophorous metal preparations of exceptionally high activity may be produced on carriers. Prior to reduction, the oxide or some other readily reducible compound of the metal is thoroughly mixed with the carrier. A perfect

admixture of the components may be attained when metal and carrier are capable of forming isomorphic mixed crystals and can be co-precipitated, as for example Ni and Mg in the form of formate, or, when the two components can form a solid compound, for instance, of the oxide-spinel type, the oxide-hydrate precipitate of which already contains the two components in homogeneous distribution. Under such conditions a metal of extremely fine distribution is formed on reduction. The presence of carrier prevents the grains from becoming coarse.

Pyrophorous metals have been successfully produced from iron, bismuth, nickel, lead and copper oxides /hydroxides/, by reduction in gasous phase with hydrogen. In some cases, the reduction may be carried out also when starting from an oxide suspension. Lower metal oxides with pyrophorous properties can be produced by the reduction in a H_2-stream of the higher oxides of multivalent metals. Thus, for instance, pyrophorous MoO_2 was obtained at 300-350°C from MoO_3; Cr_2O_3 /on carrier/ from CrO_3 at 480°C; FeO from iron/II/oxalate at 320-340°C; UO_2 from uranyl oxalate at about 400°C etc.

Pyrophorous <u>iron</u> is formed from Fe_2O_3 by reduction at 350-450°C in a hydrogen stream. Using short reduction times a pyrophorous product may be obtained at temperatures up to 600°C.

Reduction with hydrogen at 350°C of iron/II/oxalate, iron/II/tartarate, iron/II/citrate or iron/II/chloride as the starting materials also yields pyrophorous iron.

Pyrophorous <u>nickel</u> is formed in a H_2 stream by the reduction of $Ni/OH/_2$ at relatively low temperatures. $Ni/OH/_2$ may be precipitated from 10 per cent nickel nitrate with 25 per cent NaOH. The precipitate is washed free of NO_3^-,

then dried. From 150 to 200°C reduction gives a spontaneously pyrophorous product and above 250°C a latent pyrophorous product.

Reduced at temperatures below 250°C in a H_2 stream nickel sesquichloride yields a highly pyrophorous nickel preparation. Sesquioxide can be produced from basic nickel carbonate by decomposition at 350 - 450° with air.

The direct reduction of basic nickel carbonate in a H_2 stream at about 200°C gives only a latent pyrophorous product.

Nickel oxalate is reduced by hydrogen to pyrophorous nickel. A metal of stronger pyrophorous nature can be obtained when oxalate is first converted into oxide by thermal decomposition.

Pyrophorous copper is obtained by the reduction of active CuO with hydrogen at 50 - 150°C. Active CuO may be produced in the following way: Under vigorous stirring the aqueous solution of $CuCl_2$ and $NaOH+CH_3OH$, respectively, is added dropwise from two separatory funnels to water at 45°C, so as to maintain a slight excess of alkali throughout the whole procedure. After a short time, the black-brown precipitate is filtered and washed until the washing water, on acidifying with HNO_3 and on the addition of $AgNO_3$, shows no opalescence. The preparation is dried at 60°C for 12 hours. Reduction at 100°C for 20 hours yields a latent pyrophorous product.

Basic copper carbonate reduced with hydrogen at 120°C gives latent pyrophorous copper.

CuO precipitated on silica gel, when treated with hydrogen at 120°C is reduced to spontaneously pyrophorous copper.

Pyrophorous cobalt is formed from cobalt/III/ hydroxide on reduction in a hydrogen stream. The temperature has to be raised to at least 300°C. Up to about 400°C the product is a spontaneously pyrophorous, and up to 600°C a latent pyrophorous metal.

Cobalt of very high activity is obtained on Al_2O_3 carrier. The mixture of precipitate serving as starting material, may be obtained in the following way: To an $Al/NO_3/_3$ solution, under vigorous stirring a 20 per cent NaOH solution is added, until the formed precipitate dissolves. Under continued stirring, a thin jet of $Co/NO_3/_2$ solution acidified with HNO_3 is added. A precipitate is formed, which is sedimented, decanted and centrifuged. Next, the precipitate is friturated under water, then boiled. This procedure is repeated until the liquid is free of nitrate. After centrifugation, the precipitate is dried at 100°C. Reduction is carried out in the same way as in the previous case.

Also pyrophorous lead can be produced from a suitable oxide by reduction with hydrogen.

b/ Metal oxides and a few metal salts can in some cases be reduced to a pyrophorous metal by treatment with gaseous CO instead of H_2. In this way, active iron and copper was produced from oxides. It should be mentioned, however, that the use of CO may result in an irreversible adsorption, particularly in the case of transition metals.

c/ One of the important methods for the production of pyrophorous metals is the thermic decomposition of salts of organic acids. Decomposition has to be carried out under exclusion of air. This method has been used to produce pyrophorous iron from iron oxalate, bismuth from bismuth citrate, lead from lead tartrate and citrate, zinc and cadmium from the corresponding tartrates, at temperatures

of about 400°C. This method yields preparations of high activity owing to the loose structure brought about by the decomposition of anions of considerable space requirement.

d/ The decomposition of organic metal compounds also may yield pyrophorous metals. Pyrophorous iron aerosol is obtained from $Fe/CO/_6$ by decomposition in a H_2, N_2 or Ar stream at about 200°C. The pyrophorous character is preserved also in the cotton-wool-like aggregate obtained by the sedimentation of the aerosol. Carbonyls decomposed in organic solvents yield pyrophorous metals of colloidal distribution. Thus pyrophorous iron and nickel organosols are formed from $Fe/CO/_5$ and $Ni/CO/_4$, respectively.

Highly pyrophorous iron is obtained by the decomposition of solutions of iron-ethyl iodide or ethyl magnesium bromide+iron/II/ iodide.

Thermal decomposition of lead tetraethyl, $Pb/C_2H_5/_4$, yields pyrophorous lead organosol.

e/ Pyrophorous Cr, Mn, Mo, W, U, Co, Ni, Fe and Cu are obtained from the corresponding metal amalgams, if mercury is distilled off in vacuum at 350°C.

f/ Metal salts are reduced with metallic sodium in liquid ammonia. Thus pyrophorous iron, copper, cobalt, and nickel have been produced from the corresponding nitrates, manganese from iodide, copper, silver, zinc and cadmium from their complex cyanides.

g/ Among the pyrophorous substances pyrophorous Raney-nickel is of particular importance. It may be produced in the following way: From an Al - Ni alloy of 4 : 3, aluminium is extracted with 25 per cent NaOH solution. Extraction shall begin at 0°C, and at the end of the procedure the

temperature shall attain about 100°C. When the evolution of H_2 has ceased, the residue is thoroughly washed, first with alkali, then with water and finally water is removed by washing with alcohol. This Raney nickel consists of crystals of about 40 to 80 Å, which lends the material an unusually high reactivity.

h/ Pyrophorous antimony is produced at -90°C by the oxidation of SbH_3.

i/ By striking an arc between thin copper electrodes in a H_2 atmosphere /8 kV voltage/, the electrodes get pulverized. The copper aerosol thus produced is pyrophorous.

Pyrophorous zinc, manganese and tin can be prepared by arc discharge in liquid argon.

j/ Copper precipitates electrolytically from a $CuCl_2$ solution containing HCl, on addition of zinc dust /ice cooling/. After allowing to stand, the precipitate is washed and decanted a few times with water, then with methanol. The residue is dried under suction by gentle heating. The preparation contains a significant quantity of zinc which may be extracted with hydrochloric acid /ice cooling/.The colour of the powder turns from black to red, and, due to the coarsening of the product loses its pyrophorous character.

k/ When a small quantity /!/ of pure copper acetylide /prepared from an ammoniacal Cu_2Cl_2 solution and C_2H_2/ is electrically ignited in H_2 atmosphere /of about 20 Torr/ a pyrophorous copper preparation is obtained. The product is slightly contaminated with carbon.

The method of preparation, the applied temperature and reaction time determine the degree of activity of the pyrophorous preparation; in extreme cases an inadequate choice of the reaction conditions may result in an inactive product.

X-ray examinations have shown that generally pyrophorous properties are characteristic of preparations of high dispersivity. High preparation temperature or brutal subsequent heat treatment result in a coarsening of the crystal grains. No definite temperature can be given, above which the pyrophorous nature of the product will decrease or disappear, because this temperature varies from metal to metal, and is also a function of the duration of heat treatment and of the method of preparation. It was found generally that at temperatures exceeding 400 - 500°C, preparations are deactivated in a relatively short time.

When a pyrophorous iron preparation obtained by reduction of iron oxalate is exposed to a temperature of 450 - 500°C, it loses quickly its pyrophorous character. On the other hand, active iron produced from a mixture of Fe_2O_3 + Al_2O_3 preserves its pyrophorous properties even when the temperature is raised to red heat /the Al_2O_3 carrier prevents the coarsening of the grains/.

The importance of the duration of the heat treatment is illustrated by the following example: a pyrophorous iron preparation kept for 45 minutes at 600°C completely lost its pyrophorous nature, whereas on a shorter exposure to the same temperature the ability for self-ignition was maintained.

It should be mentioned here that active iron when stirred in the course of heating, loses its activity quicker and at a lower temperature than a preparation heated without stirring. Stirring promotes sintering and recrystallisation. The sintering of active iron powder formed by the decomposition of iron pentacarbonyl at 200°C can clearly be observed at 600 - 700°C, because inactivation is accompanied by a marked reduction in volume.

The decisive importance of the temperature of preparation is further proved by experiments carried out with $Ni/OH/_2$.

Reaction with hydrogen at 155°C resulted in a highly active, spontaneously pyrophorous preparation, at 235°C only a latent pyrophorous substance was obtained and at 500°C a completely inactive product.

The role of the quality of the starting material is indicated by the fact that the reduction at 300°C in H_2 atmosphere of sesquioxide produced from basic nickel carbonate by decomposition in air at 350 - 400°C yielded spontaneous pyrophorous nickel, whereas sesquioxide produced by intensive ignition /under identical conditions of reduction/ gave an inactive product.

Finally, the combined effect of reduction time and temperature is illustrated by the example of the production of a pyrophorous metal oxide. Molybdenum trioxide was reduced 120, 90 and 60 hours in a H_2 stream at 300, 350 and 450°C, respectively. In the first two cases pyrophorous products were obtained. In spite of the relatively short reduction time, the preparation obtained at 450°C proved inactive /owing to the applied relatively high temperature/. The pyrophorous nature is due to finely distributed MoO_2.

Pyrophorous lead, cadmium and zinc heated above 500°C lose their activity in a short time.

2/ Heat content, lattice structure and dispersivity of pyrophorous substances

X-ray and calorimetric investigations of pyrophorous preparations, by furnishing information on defects of the crystal lattice, on the dimensions of the elementary particles, and on differences in the heat content of pyrophorous substances and common metals, greatly contributed to a better understanding of the pyrophorous character.

Prior to X-ray examinations, it is expedient to subject the samples to a mild inactivation in order to facilitate their handling /see Part II, Paragraph D/4/.This permits to transfer the pyrophorous powder in air into thin acetylcellulose or plastic tubes and to take X-ray diagrams without the danger of self-ignition. From the broadening of the interference lines obtained for the help of preparations the average particle size can be determined. In the knowledge of the particle size the total surface area of the primary particles can be directly obtained.

In the following tables the dimensions and the total surface areas of primary particles determined by X-ray investigations are given with an indication of the conditions of preparation of the substances.

Iron

Method of preparation	Temperature of preparation °C	Particle size Å	Surface area[x] m^2/gram-atom	Pyrophorous character
Decomposition of $Fe/CO/_5$	200	81	5300	spontanously pyrophorous
Decomposition of $Fe/CO/_5$	220	90	4800	spontanously pyrophorous
Decomposition of $Fe/CO/_5$	650	100 000	4	not pyrophorous

[x] In the calculation of the surface the primary particles were assumed to be cubical

Nickel

Method of preparation	Temperature of preparation °C	Time hour	Particle size Å	Surface area m^2/gram-atom	Pyrophorous character
$Ni/OH/_2$, reduction with H_2	155	35	103	3823	spontaneously pyrophorous
Nicel sesquioxide, reduction with H_2	235	35	115	3425	spontaneously pyrophorous
Basic nickel carbonate, reduction with H_2	200	35	149	2643	latent pyrophorous
Basic nickel carbonate, reduction with H_2	475	24	266	1480	not pyrophorous

Copper

Method of production	Temperature of production °C	Time hour	Particle size Å	Pyrophorous character
Cu precipitated from $CuCl_2$ solution with Zn dust	2-3	-	48	Spontaneously pyrophorous
Reduction with H_2 of CuO deposited on Fe/III/ oxyhydrate	100	16	75	Spontaneously pyrophorous
Reduction with H_2 of CuO deposited on silica gel	120	20	120	Spontaneously pyrophorous
Reduction of basic Cu-carbonate with H_2	120	24	180	latent pyrophorous
CuO reduced with H_2	100	20	185	latent pyrophorous
CuO reduced with H_2	250	2	10,000	not pyrophorous

The broadening of the interference lines /particularly in case of indexes of higher order/ may be due not only to the minute crystalite dimensions, but also to some defect of the crystal lattice. Both these causes manifest themselves in the form of excess energy content of the same order of magnitude /a few cal/g atom/. /Difference in energy content between the states of common and pyrophorous metals./

The extent of the lattice defect can be calculated from the intensity distribution of X-ray interferences. The X-ray investigation of the majority of pyrophorous substances shows anomalies in the lattice: the lattice gravity centres of the atoms deviate by about 10^{-1} Å from the positions occupied in the regular lattice.

The average amplitude of the defect, a quantitative characteristic of such anomalies in the lattice, was found to be 0,076 Å for pyrophorous iron, 0,055 Å for nickel, and 0,15 Å for copper /on iron oxide carrier/, from a number of tests carried out on pyrophorous preparations. Using Debye's corresponding "characteristic temperatures" the following values were obtained for the "corresponding defect temperatures" on the basis of these average amplitudes of defect: Fe : 566° abs.; Ni : 525° abs. and Cu : 1100° abs. This means that the preparation subject to lattice defects behaves in the same manner as a metal of normal lattice heated to the temperatures mentioned above.

The integration of the specific heat of the metal between 0 and the "corresponding defect temperature" gives the excess heat content caused by the lattice defect /strictly speaking only half of this value will be considered/, as corresponding to the potential part of the heat content, while the other half is of kinetic origin/. Potential excess heat content for three metals mentioned above is: Fe : 1,45 kcal/atom; Ni : 0,43 kcal/g atom; Cu : 3,24 kcal/g atom.

It is to be emphasized again that the values indicated above for the "amplitude of defect" for the "corresponding defect temperature", and for the "excess heat content" may greatly vary with the method and the conditions of preparation. Considering the strong inclination of metals to crystallization, it may be assumed that aggregates obtained through condensation from pyrophorous iron aerosols have lattice structures free of defects. This assumption has actually been proved by the electron diffraction patterns i.e. small crystallite dimensions do not broaden electron interference lines, whereas lattice defects result in a broadening of these lines.

The difference in heat content of pyrophorous and common metals can be investigated also by calorimetry. Excess heat content determined by this method may be due both to lattice defects and to high dispersivity, whereas X-ray examination discloses only excess heat content resulting from lattice defects. The difference in excess energy determined by X-ray and by calorimetric investigations can be attributed to the large specific surface area of pyrophorous substances.

The excess heat content in pyrophorous materials established by calorimetry may be defined also as the difference in the heat of solution of active and normal metals. The excess energy thus defined is naturally highly dependent also on the methods and conditions of production. The following numerical values determined by calorimetry give an indication on the order of magnitude of the discussed excess energies: Fe : 1,4 kcal/g atom, Ni : 1,8 kcal/g atom, Cu : 3,0 kcal/g atom.

3/ The causes of pyrophorous nature

The most widely used method for the production of pyrophorous preparations is the reduction in a hydrogen stream. Hence the interpretation of pyrophorous nature according to which the

high activity connected with pyrophorous character is due to dissolved hydrogen, a residue of the reduction. According to this concept, hydrogen atomically bound, on the surface of the preparation brought into contact with air, enters into reaction with oxygen under liberation of a significant amount of heat. Local liberation of heat starts the combustion of the whole preparation. This interpretation seems to be supported by the observation that pyrophorous iron inactivated by the adsorption of CO_2 recovers its activity in a hydrogen stream. However, the finding that a preparation kept several hours in a nitrogen stream free of oxygen and at a temperature of about 200°C does not lose its spontaneously pyrophorous properties, in spite of the fact that under these conditions hydrogen possibly bound on its surface is most certainly removed, is in contrast with this conception. Contradictory to this interpretation is further the fact that pyrophorous products may be obtained also by the decomposition of metal compounds, for instance of $Fe/CO/_5$, though a possible presence of hydrogen is excluded in this case.

The state of the metal is to be considered as the true cause of pyrophorous nature which, on the basis of calorimetric and X-ray investigation is correlated with the higher energy content of pyrophorous materials. Pyrophorous behaviour may be the result of an exceptionally large free surface or of lattice defects. Both factors are manifested in the form of excess energy of the same order of magnitude /a few kcal/g atom/. Depending on the conditions of production, one or the other of these causes may prevail or even attain an exclusive role. It should be noted, however, that extremely small crystallite dimensions as cause activity could be detected in all pyrophorous preparations examined so far, whereas considerable lattice defects have been revealed only in a few cases. For example, highly pyrophorous iron, produced by the decomposition of $Fe/CO/_5$ in the gaseous phase, has a crystal lattice free of defects, provided the conditions of sedimentation have been adequately chosen.

A direct correlation between pyrophorous nature and fineness of particles is established by the mechanism of self-ignition suggested by G. Tamman. According to the proposed mechanism, the metal in contact with air is coated with a surface film of oxide, while liberating an equivalent quantity of heat. The rise in temperature of a preparation is directly proportional to the specific surface area of the metal. If the particles are extremely small /as is the case with pyrophorous preparations/, the large quantity of liberated heat causes self-ignition, and the metal is generally oxidized to its possible oxide. On the basis of this it is easy to understand why a heat treatment at a sufficiently high temperature or a high temperature of reduction applied in the preparation result in the formation of coarser particles and thus in inactivation. Owing to the reduction of free surface as a consequence of heat treatment, surface oxidation does not develop sufficient heat to bring about a spontaneous self-ignition of the preparation.

Magnus also attributes the pyrophorous nature of metals to particularly fine particle dimensions. In his opinion, the heat of adsorption of atmospheric oxygen may lead to self-ignition.

Methods developed for the mild inactivation of pyrophorous metals are completely in accordance with the explanation of the pyrophorous nature given above.

4/ Mild inactivation of pyrophorous metals

The handling and testing of pyrophorous materials are rendered very difficult and in many cases even impossible by the circumstance that they are to be kept protected from air /in vacuum or in an oxygen-free atmosphere/. In order to facilitate their handling active metals are usually subjected to a certain degree of inactivation, owing to which "spontaneously" pyrophorous materials are converted to a "latent" pyropho-

rous form. On mild inactivation the metals do not lose their catalytic activity and adsorption power and very probably do not undergo any significant changes in structure or distribution, only their surface gets coated with a thin protective film which protects them from burning when coming into contact with oxygen. Therefore, a sharp distinction has to be made between the inactivation techniques discussed in this chapter and inactivation brought about by a heat treatment which implies the loss of the fine grain structure and the disappearance of all activity connected with pyrophorous behaviour. Preparations obtained by mild inactivation preserve in air for years their latent pyrophorous nature.

Formerly protective coatings were formed by immersing and opening the vial containing the pyrophorous preparation in the solution of a suitable film - forming for instance in a 0,5 per cent solution of acetyl callulose in acetone, or in a diluted solution of polystyrene in benzene, - and by evaporating subsequently the solvent /this operation is carried out already in air and the temperature can be raised up to 50°C without any risk of self-ignition/.

Later it was discovered that the same protective effect can be obtained if the pyrophorous preparation is carefully mixed with a volatile liquid, free of film-forming agent, which does not react with the preparation for instance with benzene, 96 per cent or anhydrous alcohol or acetone and the solvent is then slowly evaporated from the wet paste. It was further shown that contrary to a sudden contact of the active metal with air, a slow contacting, for example by diffusion, does not cause self-ignition, but provides for a protective inactivation.

It has been investigated whether O_2 still present in the inactivating liquid may be responsible for the disappearance of the spontaneously pyrophorous nature. Results show that

inactivation can be attained also with pure hydrocarbons, for instance, with petroleum ether, even if atmospheric oxygen has been previously completely removed from the hydrocarbons by thorough boiling under reflux and simultaneous introduction of H_2 or/and N_2 free of oxygen.

Experience unequivocally shows that inactivation is due to the fact that on evaporating the solvent, atmospheric oxygen comes only slowly into contact with the surface of the material and thus gradually a thin oxide surface layer is formed /slow heat evolution excluding self-ignition/, which protects the coated material from further oxidation. As the preparation preserves its fine grained structure and the possible defects in the crystal lattice, local heating /e.g. touching with a hot wire or with a burning wooden stick/ will cause its burning to oxide under luminous phenomenon.

X-ray diffraction tests have shown that pyrophorous iron powder obtained by the decomposition of iron pentacarbonyl, when exposed to slow diffusion of air, gets coated with a protective oxide layer of the composition Fe_3O_4. It has been established by X-ray diagrams and chemical analysis, that the thickness of the layer is 9 Å.

5/ Pyrophorous properties and reactivity

It is clear from the above said that the energy content of pyrophorous metals is higher than that of common metals; the small grain size and the irregular lattice structure result in a very high reactivity. This high reactivity is manifested by the property, which, at the same time, is the criterion of pyrophorous character, that in air a pyrophorous preparation will take fire and burn to an oxide at room temperature or at a relatively low temperature. Thus, pyrophorous metals burn at lower temperatures than usual.

Even at the time when pyrophorous behaviour was first discovered, it was observed that pyrophorous metals of higher activity decompose water already at room temperature. Active U, Mn and Fe behaved in this manner. The capacity to decompose water is highly dependent on the method and on the temperature of preparation of the pyrophorous substance. An iron preparation obtained at relatively low temperatures by the reduction of iron oxalate shows a tendency to decompose water already at $10^{\circ}C$ and at $50^{\circ} - 60^{\circ}C$, decomposition becomes vigorous. The reaction with water is particularly vigorous on an Al_2O_3 carrier, that is to say, when the metal has been prepared by the reduction of a mixture of Fe_2O_3+ $+Al_2O_3$.

Pyrophorous metals have played a significant role in the history of the production of metal carbonyls. Owing to the high dispersivity and reactivity of pyrophorous metals, they form readily the corresponding carbonyls. Iron pentacarbonyl was first produced from pyrophorous iron. Similarly, $Mo/CO/_6$, $W/CO/_6$ and $Fe/CO/_5$ were successfully obtained from the corresponding pyrophorous metals.

Pyrophorous metals have a particularly high adsorptive power. Adsorption of H_2 and CO_2 by active Fe, Co and Ni and the adsorption of NH_3 by Fe and CO have been investigated in detail.

These investigations have also shown that in the presence of a carrier the adsorptivity is increased and diminishes at a slower rate with time.

In some cases an exceptionally high absorbing capacity for hydrogen was found. For instance, pyrophorous nickel adsorbed 100 volumes of hydrogen per unit volume; cobalt 48 times its own volume of hydrogen. These figures, however, proved to be unreliable and the high hydrogen uptake was partly attributed to the presence of oxides.

Pyrophorous metals and metal oxides are of practical importance primarily on account of their catalytic activity. The catalytic properties of pyrophorous metals in hydrogenation, and particularly those of nickel, are common knowledge. It should be noted, however, that opinions differ as regards the importance of the pyrophorous nature of Ni catalysts: some authors maintain that the activity of pyrophorous nickel catalyst in hydrogenation reactions is not higher than that of non-pyrophorous nickel.

The reduction of phenol to benzene by hydrogen under atmospheric pressure is efficiently catalysed by molybdenum trioxide. Detailed investigations have shown that actually the reaction is catalysed by active MoO_2. When plotting the activity versus time, curves showed first an increase in catalytic activity at about 400°C up to a maximum value /indicating that the actual catalyst is formed by a reduction of the trioxide/, after which a decrease in the activity was observed /owing to the sintering of the catalyst and the coarsening of the grain size/. A definite parallelism could be observed between the catalytic activity of MoO_2 and its pyrophorous properties. Catalytically active MoO_2 is pyrophorous, while inactive MoO_2 is not pyrophorous.

It has been observed that ZnO and Cr_2O_3 catalysts used in the synthesis of methanol, coming into contact after use with air, warmed up. /Possible manifestation of their pyrophorous nature!?/

The possible fields of application of pyrophorous metals have not been sufficiently exploited so far. Thus, little consideration was given to the use of pyrophorous metals in organic syntheses.

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E./ DEFINITIONS OF CHARACTERISTIC PHYSICAL AND PHYSICO-CHEMICAL VALUES

Density	Mass per unit volume /m . v^{-1}/.
Specific gravity	Weight per unit volume /m . g . v^{-1}/. Abbrev.: Spec. grav.
Relative density	Density referred to the density of water of a specified temperature /usually 4°C/.- The numerical value of the specific gravity and the relative density are equal, as the density of water under reference is 1. Abbrev.: d_4^{20}
Molecular weight	Sum of the atomic weights of the atoms forming the molecule. Abbrev.: M.w.
Melting point	The constant temperature at which the solid and liquid phases of a pure substance are in equilibrium. Melting point varies with ambient pressure. Substances are generally characterized by their melting point appertaining to 1 atm ambient pressure /760 Torr/. Abbrev.: M.p.
Boiling point	The temperature at which the vapour pressure of a pure liquid equals the external pressure. The boiling point is a function of atmospheric pressure /BP/. Substances are generally characterized by their boiling point appertaining to 1 atm /760 Torr/ ambient pressure. At pressures differing from this value pressure will be indicated in mm Hg. Abbrev.: B.p.

Tension curve — A curve showing saturated vapour pressure in dependence of temperature.

Enthalpy — /called also heat content/ A thermodynamical value defined by the equation $H = E+p \cdot v$ /H = enthalpy, p = = pressure, v = volume, E = intrinsic energy/. Enthalpy at 25°C and under one atmosphere pressure is called "standard enthalpy". /$H^{\circ}_{298,16}$/.

Heat of fusion — Quantity of heat adsorbed when a certain unit of solid substance /usually 1 g or 1 mole/ is changed to a liquid at constant temperature.

Heat of vaporization — Quantity of heat absorbed by the system at a given temperature, when a certain unit /usually 1 g or 1 mole/ of liquid is transformed into vapour of the same temperature.

Heat of formation — The quantity of heat evolved or absorbed when a compound is formed from its elements at a given temperature. Enthalpy of formation related to one atmosphere of pressure and 25°C temperature is called "standard heat of formation".

Heat of combustion — The total change in enthalpy accompanying the complete combustion of a specified quantity /usually 1 g or 1 mol/ of the compound.

Entropy — A thermodynamic concept, the value of which is depending on the heat content and temperature of the body. During a reversible isotherm change the increase in entropy of a system / Δ S/ equals the ratio of the

amount of heat entering /Δ H/ to the temperature at which the heat is adsorbed:

$$\Delta S = \frac{\Delta H}{T}$$

Entropy appertaining to 25° C of temperature and one atmosphere of pressure is called "standard entropy" /$S^{o}_{298,16}$/.

Critical temperature — The temperature above which a given gas cannot be liquefied by an increase in pressure alone.

Critical pressure — The pressure required for the liquefaction of a given gas at the critical temperature.

Critical density — The quantity of material per unit volume at the critical pressure and temperature.

Viscosity /dynamic/ — The measure of resistance of a fluid to flow. It may be defined as the tangential force acting on the unit surface of two horizontal planes at unit distance from each other, when the space between the two planes is filled with the material in question and one of the planes is stationary, while the other is moving at unit velocity. Dynamic viscosity /η/ is the combined measure for adhesion and cohesion. Its unit is the Poise /P/=g/cm.sec; 0,01 Poise = 1 centipoise /cP/.

Kinematic viscosity — The ratio of dynamic viscosity to density /η /S/. Its unit is the Stoke /S/; 0,01 Stoke = 1 centistoke /cS/.

Refractive index — The absolute refractive index is the velocity of propagation of the light in va-

cuum, divided by the velocity of propagation of the light in the medium under consideration. Refractive index is a function of temperature, wavelength and pressure. The relative refractive index is the quotient of the velocity of propagation of the light in two different media.

Heat of formation and heat of reaction

The heat of formation /enthalpy of formation/ is the change in enthalpy /heat of reaction/ accompanying the formation of 1 mol of the compound from its elements. When giving the enthalpy of formation, the state of the substance is to be indicated. Distinction is made between "normal enthalpy of formation" /referring to p = 1 atmosphere of pressure and arbitrary temperature/: ΔH_T°, and "standard enthalpy of formation" /p = 1 atmosphere and 25°C temperature/: ΔH_{298}°. The normal heat of formation of a compound is:

$$\Delta H_T^\circ = H_T^\circ \text{ /compound/} - \sum H_T^\circ \text{ /element/.} \qquad /1/$$

According to cenvention, the standard heat of formation of the elements is zero. Tables generally give the values of the standard heats of formation, and usually contain also the empirical functions of specific heat, which permit the conversion of the heats of formation for another temperature.

When calculating the heat of reaction or the heat of conversion, the sum of the heats of formation of the reactants is subtracted from the sum of the heats of formation of the formed compounds:

$$\Delta H_T^\circ/\text{conversion}/ = \sum \Delta H_T^\circ/\text{formed compound}/ - \sum \Delta H_T^\circ/\text{reacting compound} \qquad /2/$$

Standard heats of formation or heats of reaction are seldom satisfactory, because processes are generally carried out at temperatures other than 25°C. For conversion, the following equation is used:

$$\Delta H_T^o = H_{298}^o + \int_{298}^{T} \Delta C_p dT, \qquad /3/$$

where C_p is the difference between the sum of the specific heats of the formed compounds and the sum of the specific heats of the reacting compounds.

The value of the integral in Equ. /3/ can be determined graphically, by plotting the values of temperature on the abscisse and those of C_p on the ordinate. The value of the integral is represented by the area delimited by the curve of specific heat, the ordinates 298 and T and the abscisse axis.

An approximative method for the calculation of the heat of formation or heat of reaction for temperatures other than 25°C is based on the empirical formulae of the functions of specific heat. These formulae have the following form /tabulated constants are available in literature/:

$$C_p = a + bT + cT^2 + .. \qquad /4/$$

or

$$C_p = a + bT + \frac{c'}{T^2} . \qquad /4'/$$

On integrating the function of specific heat according to equations /4/ and /4'/, the dependence of enthalpy on temperature is given by the following equations:

$$H_T = H_o + aT + \frac{1}{2} bT^2 + \frac{1}{3} cT^3 + .. \qquad /5/$$

or

$$H_T = H_o + aT + \frac{1}{2} bT^2 - \frac{c'}{T} \qquad /5'/$$

where H_o is the "hypothetic" value of the enthalpy at absolute zero temperature. Accordingly, heat of conversion at T^o is given by the following formula:

$$\Delta H_T^o = \Delta H_{298}^o + \Delta a/T-298/ + \frac{\Delta b}{2} /T^2 - 298^2/ + \frac{\Delta c}{3} /T^3-298^3/$$

$$/+.. \qquad /6/$$

or

$$\Delta H^oT = \Delta H_{298}^o + a/T-298/ + \frac{\Delta b}{2} /T^2-298^2/ - \Delta c'/\frac{1}{T} - \frac{1}{298}/ \qquad /6'/$$

where Δ a, Δ b, Δ c, and Δ c' are differences of constants characteristic for the reacting substances.

In many cases, empirical power series are unsatisfactory for an adequately accurate description of the complicated dependence of specific heat on temperature, and it is becoming customary, therefore, to give in tabular form directly the values of the specific heat or the molar heat of the substances for different temperatures. The use of these tables is not as simple as that of the power series expressions, but difficulties may mostly be eliminated with the help of Ulich's approximations.

The first approximation of Ulich considers enthalpy as independent of temperature, and uses the standard enthalpy value in calculations at various temperatures. This approximation involves substantial errors at temperatures differing considerably from 25°C.

The second approximation of Ulich makes already allowances for the dependence of enthalpy on temperature, by using for the calculations the specific heat pertaining to 298°K. According to this approximation, the enthalpy of conversion at T^oK is:

$$\Delta H_T^o = \Delta H_{298}^o + /T-298/ \Delta C_{p,298} \qquad /7/$$

Essentially also the third approximation of Ulich is based on equation /7/. However, it takes also the temperature dependence of the molar heats into account in as much as the corresponding mean values are used in the calculations:

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \Delta \bar{C}_p$$

The average values of specific heat are tabulated or may be determined for example in the following way:

up to	500°K	$C_p = C_{p,300}$
from 550 to	1000°K	$C_p = \frac{1}{2} /C_{p,300} + C_{p,600}/$
from 1000 to	2000°K	$C_p = \frac{1}{4} /C_{p,300} + 2C_{p,600} + C_{p,1200}/$
from 2000 to	3000°K	$C_p = \frac{1}{6} /C_{p,300} + 2C_{p,600} + C_{p,1200} + C_{p,2400}/$

This approximation of average specific heat is based on extensive experience, though it does not represent by far the only possibility.

By the use of Ulich's approximations, the calculation of the heat of conversion for temperatures other than 25°C becomes relatively simple. The accuracy of the approximations is satisfactory for dealing with almost all industrial problems.

In thermochemical computations discussed in the following, the third approximation of Ulich has been used.

From the point of view of thermodynamics, a reaction is considered as spontaneous, if the affinity is positive. The more

positive the affinity, the greater the driving force of the reaction.The normal affinity of the reaction is equal to the difference in chemical potential of the formed and the reacting substances. The evaluation of the possibility of reactions should be based,therefore, on the chemical potential of the participating substances /this question cannot be discussed here in detail/, but generally, in the case of reactions proceeding at not very high temperatures in condensed phase, the possibilities of the reaction may be predicted correctly on the basis of the heat of reaction /i.e. the Berthelot-principle is more or less realized/.The Berthelot-principle states that the driving force of a reaction is the exothermic heat of reaction, i.e. only exothermic reactions will proceed spontaneously, and the greater is the possibility of a reaction, the greater is the amount of the heat evolved. It should be kept in mind, however, that the affinity of the reaction will be identical with the heat of reaction only at the absolute zero point, and at all other temperatures the exact decisive factor is the difference in chemical potentials.

III. EXPERIMENTAL PART

PROCESS FOR THE PRODUCTION OF FURAN FROM FURFURAL BY VAPOUR-PHASE HETEROGENEOUS CATALYSIS

A/ GENERAL

1. General instructions for work in the catalytic laboratory

A general knowledge of laboratory practice is a precondition of work in the catalytic laboratory. Among the regulations to be observed in a laboratory, safety rules and fire protection are of special importance. Keeping in mind that a catalytic laboratory involves more electrical equipment than the usual chemical laboratories, students must be definitely acquainted with the basic protection against electric shock and with safety measures for its prevention. Naturally, laboratory equipment meets the specifications of electric appliances. Similarly, those working in the laboratory must be familiar with the safety measures pertinent to the materials to be used.

Before the beginning of laboratory work, practicants must undertake the following tasks:

a/ Get acquainted with the problem set in the exercise;

b/ Study the principles of operation and the handling of the apparatus necessary for carrying out the exercise;

c/ Prepare the materials needed for the experiment;

d/ For the recording of the experimental results get ready a record sheet, previously entering into it the physical constants of the materials to be used in solving the problem and formed in the course of the work, and a short description of the process.

e/ Before starting the exercise, the team carrying out the task should divide the work among themselves. Expediently one of the students will supervise the feed, the other the tem-

perature, and the third will keep the records.

f/ All particulars should be recorded, which are necessary to reproduce the experiment, whenever wanted. All data characteristic of the process /quality and quantity of materials, physical parameters, observations, experiences/ should be recorded. When evaluating experimental results, recorded data shall be subsequently closed with evaluating comments.

g/ In order to facilitate the solution of technical problems possibly arising in the course of the experiments a technician should always be at disposal.

h/ If, in a heterogenous catalytic conversion carried out under pressure, the reactor is to be connected with equipment made of glass, a safety net, protecting from injury in case of a possible explosion, is to be placed before the glass equipment.

i/ After finishing the work, the quantities and the physical characteristics of the formed products are determined, the products purified, the apparatus is cleaned and, if necessary, the catalyst is regenerated.

j/ The textbook containing the description of the apparatus and of the experiments gives all the required information for carrying out the work and should be, therefore, thoroughly studied. As the fundamental principles of the technique are not repeated in the chapters describing the individual chemical reactions, it is advisable to consider the textbook as a comprehensive entity and to aim to master it in its entity.

2. The handling of contact catalytic apparatus

When carrying out preparative experimental work in organic chemistry the experimenter must possess a thorough knowledge of the actual chemical, physico-chemical and physical changes

that occur. This rule applies in an increased degree to our present apparatus, as it is more complicated, expensive and a sensitive instrument for chemical reactions, and those handling it must be aware of an increased moral and material responsibility. Though our equipment is rather complicated, by a thorough study of its system handling will prove easier than expected. Only when all the chemical and physical processes have been mastered, a technical knowledge of the apparatus has been acquired and the location of instruments and switches is well known, should the actual work begin. The operation of the instruments should always be checked, or else, conclusions drawn from the experiments may be misleading. Conscientiousness is essential in this work. Work with one unit of equipment should be divided between two or three persons. When determining parameters, only one of the factors shall be varied at a time, because otherwise results cannot be evaluated.

Heating may be started at maximum wattage with the aid of the toroid transformer and, after heating up, regulated to a lower performance.

Laboratory reactors working at a few tenths of atmosphere of overpressure usually do not imply any hazard of explosion, and in the event of a possible explosion, the internal construction of the reactor /aluminium block, ceramic and heat insulating layers, external jackets/ generally offers sufficient protection.

In the preparation of several catalysts, ammonium nitrate forms and if it is not washed out, it may lead to an explosion the vehemence of which depends on the residual quantity of ammonium nitrate. An explosion may occur also if clogging remains unobserved or no attention is paid to the pressure alarm and feeding is continued.

Heat effect accompanying the reactions depends on the sign and the quantity of the heat of reaction, on the dimensions of the reactor and on the parameters of the feed. A tube heated by an uniformly wound resistance wire will have a lower temperature at the two ends because of more intensive cooling. Uneven distribution of temperature will result in an uneven efficiency of the catalyst and thus of the rate of the reaction. Due to the above mentioned factors, the longitudinal distribution of the heat evolved during the reaction will not be uniform, causing irreproducible conditions. Therefore, reactor walls must be maintained at uniform temperatures. This may be attained with independently regulated individual heating sections. This permits the realization of an arbitrary temperature program along the reactor. In exotherm reactions temperatures will be higher along the axis of the reactor and in endotherm reactions the wall will have a higher temperature.

3. Feeding of the reactants into the reactor
Feeding of liquids

a/ Dripping from a burette is used when the feeding zone is free of internal pressure. If the internal space is connected with the space above the meniscus of the liquid in the closed burette, feeding can be carried out both in vacuum and under pressure. Also this method, however, has the disadvantage that the feed rate is a function of the actual hydrostatic pressure. This becomes evident from the following: If a cross section /q/ is established in the needle valve of the liquid column of a height of n cm to obtain the desired feed rate χ = volume of liquid per time, at a constant value of q χ will remain constant only if also n were constant. This latter value, however, decreases gradually from the initial 100 per cent.

b/ Fine feeding device. In the case of a liquid column of a height of 1 m the upper air space of the burette will be

kept expediently under a pressure of about 2 atm. In this case against the drop of pressure from 100% to zero only a pressure drop from 100 to 95 per cent will occur and thus error will be reduced. Evidently, the higher the pressure above the liquid to be fed in as compared to the hydrostatic pressure, the lesser the error due to the change in hydrostatic pressure. Our catalytic laboratory includes also a fine feeding device of this type.

c/ Fine feeding systems using a hypodermic syringe. With clockwork lowering of an uniform rate the weight attached to the piston also proved satisfactory. The steadily sinking piston provides an even feed.

d/ Piston-type feed devices /Fig. 19/ may be adjusted to supply the required liquid volume/time feed rate by varying the speed of revolution, the stroke length and the piston cross section. By choosing an adequate material for the wall, resistance to the corrosive effects of particular liquids may be attained. Feeding devices for reactors operating under high pressures within the range from 300 to 1000 atm may be obtained by increasing the fineness of the grinding.

Catalytic processes are sensitive to the parameters of the reaction thus to the uniformity of feed. Therefore, pumps will be devised expedient for an excess of resistance to feed pressure.

e/ The mercury fine feeding device /Fig. 20/ operates in the following way: The mercury tank is raised to a height of 1 m. Through the bottom orifice of the burette connected to the tank by a vacuum rubber tube, the laws of communicating vessels come into force. The liquid to be fed is poured into the burette over the mercury. When the tank is lifted the meniscus of the mercury in the burette drives the overlayered liquid through an overflow into the reaction space. The end

1. Motor
2. Driving disc
3. Pump drive
4. Flare joint
5. Feeding burette
6. Pressure capillary

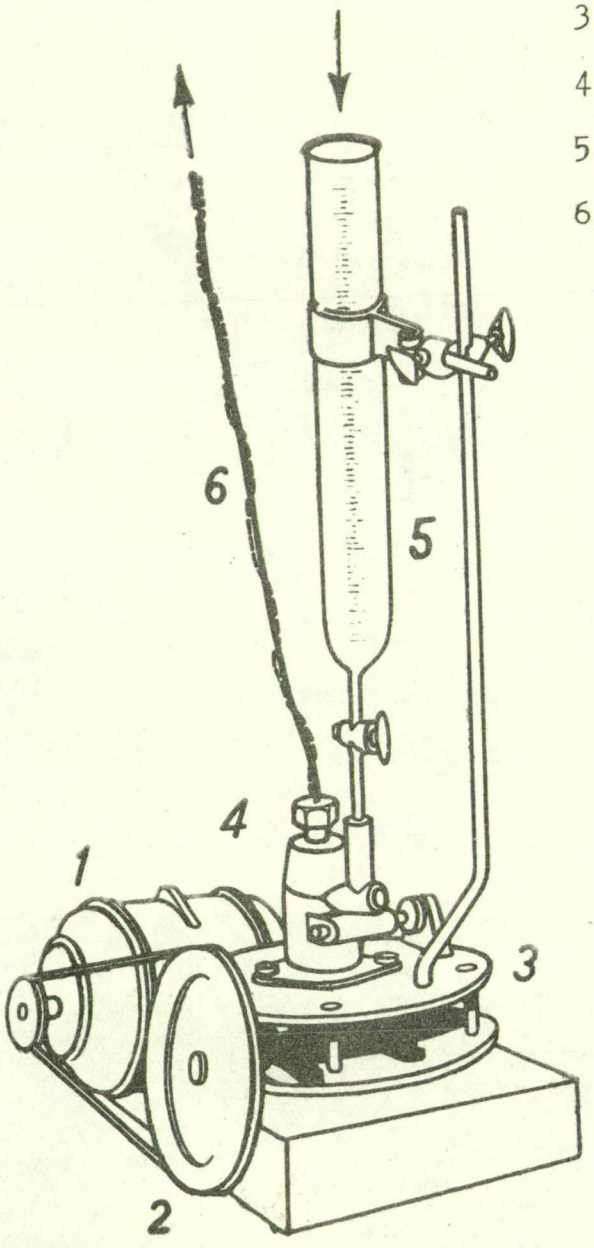


Figure 19
Piston type feeding device

A Burette

B Vacuum rubber tube

C Mercury tank

D Lift

E Spindle

F F'Mounting

H H'Gearbox

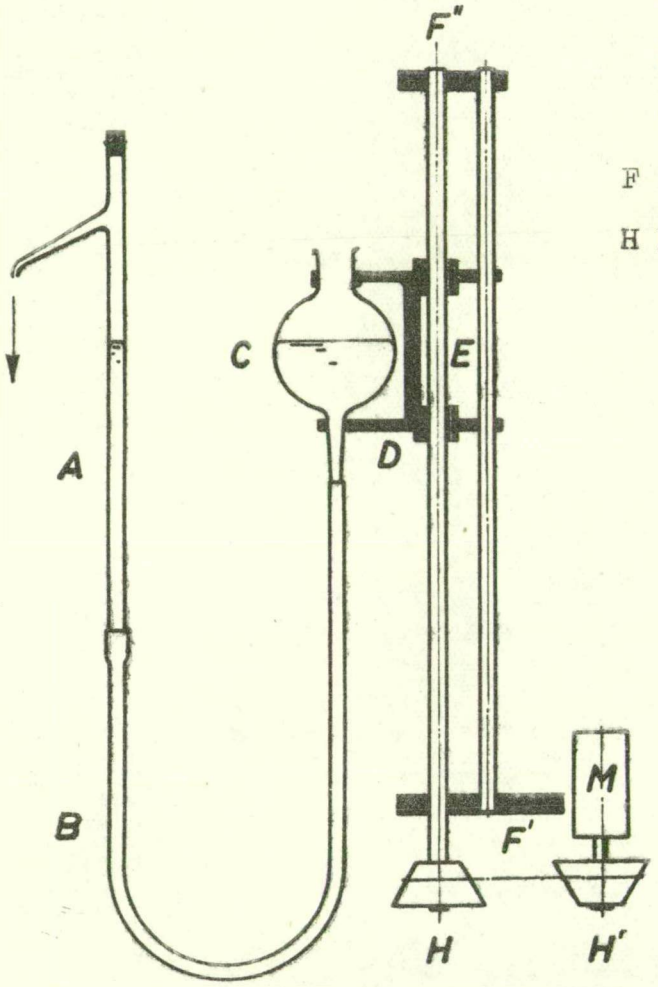


Figure 20

Mercury fine-feeding device

of the overflow is drawn out to a sharp point, which contacts the wall of the feeding vessel. Thus the drop error is eliminated and the substance is fed in in form of a film. The feeding device shown in Fig. 20 can be operated at different speeds to lift the mercury tank in 1/2, 1, 2, 4, 8, 16 or 24 hours to a height of 1 m. By decreasing the cross-section of the burette smooth fine feeding can be improved to the highest fineness. The device may be used for feeding rates within the range from 0,2 to 50 ml/h.

Feeding of solids

Solids may be fed under heating through the described feeding devices, or dissolved in liquids neutral to the reactants or by evaporation.

Feeding of gases

a/ Gases are passed from a gas bomb, or from a buffer tank of possibly large volume, following a compressor through a pressure reducer into a smaller buffer tank to establish constant pressure. Feeding this buffer tank may be adjusted with the help of our fine needle valve, equipped with a vernier, to the desired value. The rate of the gas flow is measured at low values with a differential pressure gauge, at higher values with a rotameter. For every kind of gas an individual calibration curve has to be plotted, and calibration curves for the same gases hold true only in case of identical pressure. If, for example, internal gas resistance and pressure increases in the reactor, due to carbon deposition, the calibration curve becomes void. Differential pressure gauges, equipped with micrometer screws permitting the adjustment of reproducible cross sections are to be used. Even for the same gas several calibration curves are to be plotted at different pressures.

b/ Hydrogen pumps. When conversion is poor, for instance in hydrogenation, the unconverted gas has to be recirculated. For this purpose gas pumps are utilized. Bellow-type gas pumps with concentrical rings, made of brass trumpet sheet, were found to be suitable.

c/ Membrane pumps. For feeding gases in small quantities, also vibration-operated membrane pumps may be used /Fig.21/.

1. Electromagnet
2. Vibrating reed
3. Membrane
4. Air inlet
5. Air outlet

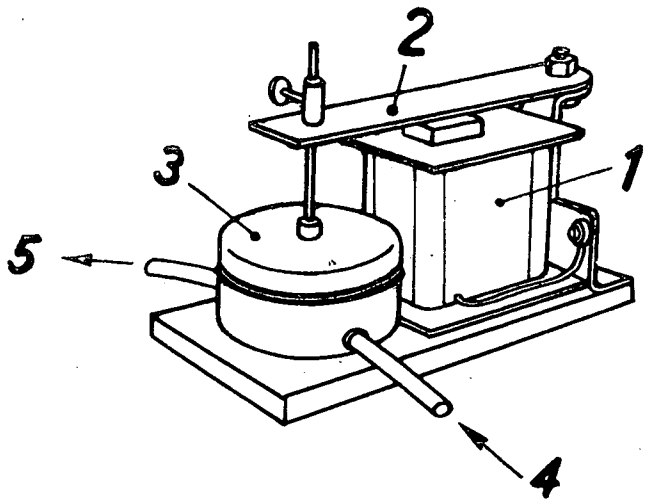


Figure 21

Membrane gas feeding pump

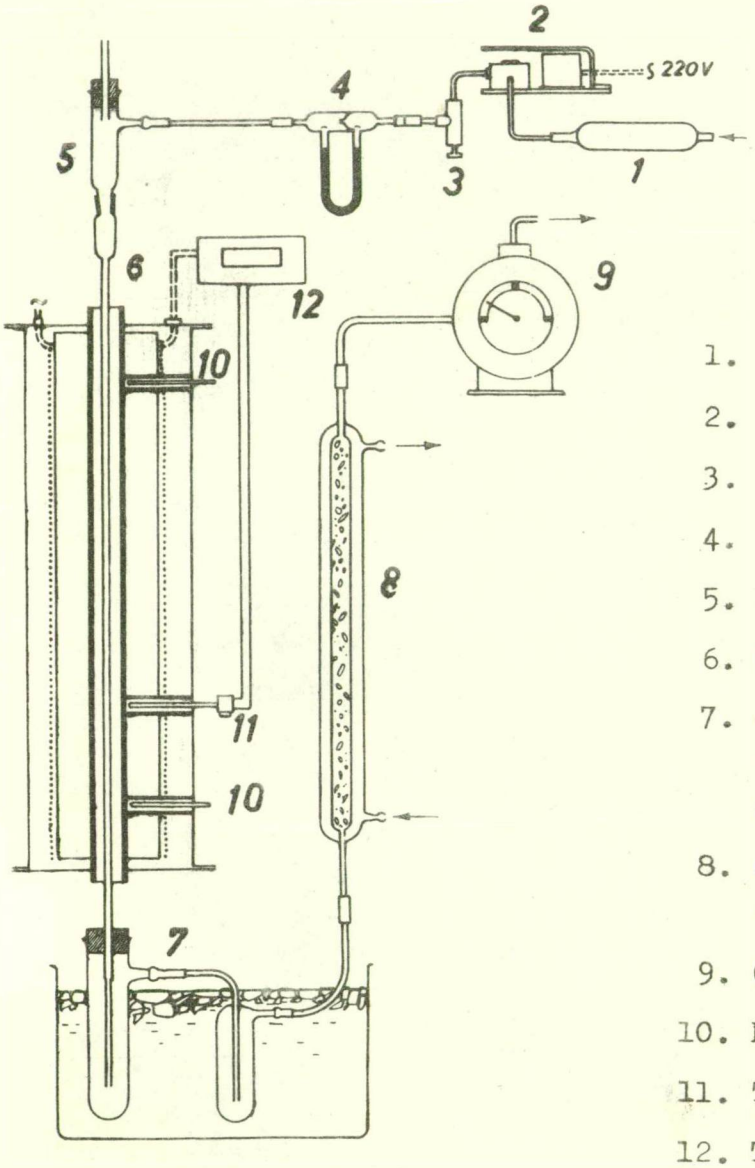
B/ EXPERIMENTAL EQUIPMENT FOR THE PRODUCTION OF FURAN

1. Experience gained with various types of reactors

The present design of our gas-phase heterogeneous catalytic laboratory is based on experiences with several types of equipment. The discussion of the problems met in the course of the development work may bring a better understanding of our equipment, therefore, some of the characteristic development steps in our experimental work will be outlined here.

The elimination of undesirable catalytic wall effect was first attempted by using a glass reactor /Fig. 22/. Through a glass drying tube filled with dry coarse calcium chloride, air is forced by a vibrator actuated membrane pump through a needle valve and a differential pressure gauge into the upper evaporating zone of the glass reactor. Furfural introduced at the top is evaporated by the heat of an infrared lamp on ceramic beads, then enters a Raschig-ring system to blend with the air and passes downwards through the reactor coming into contact with the catalyst. In the mixture of salt and ice condensable substances /unconverted furfural, water, etc./ are condensed, while gases containing mainly nitrogen, carbon monoxide, carbon dioxide and furan pass through a small cooled active carbon column. Furan is adsorbed and residual gases exit through a gasometer. The glass reactor tube is encased in an iron tube embedded in an aluminium block, equipped with electric heat regulation. In this equipment the contact between the glass reactor tube and the iron tube was not uniform. Therefore, local overheating, difficult to eliminate, may occur. Important differences in temperature between evaporator and reactor unit frequently resulted in breaks.

These difficulties in heat transfer arise also when using quartz instead of glass. The evaporator being on top, the

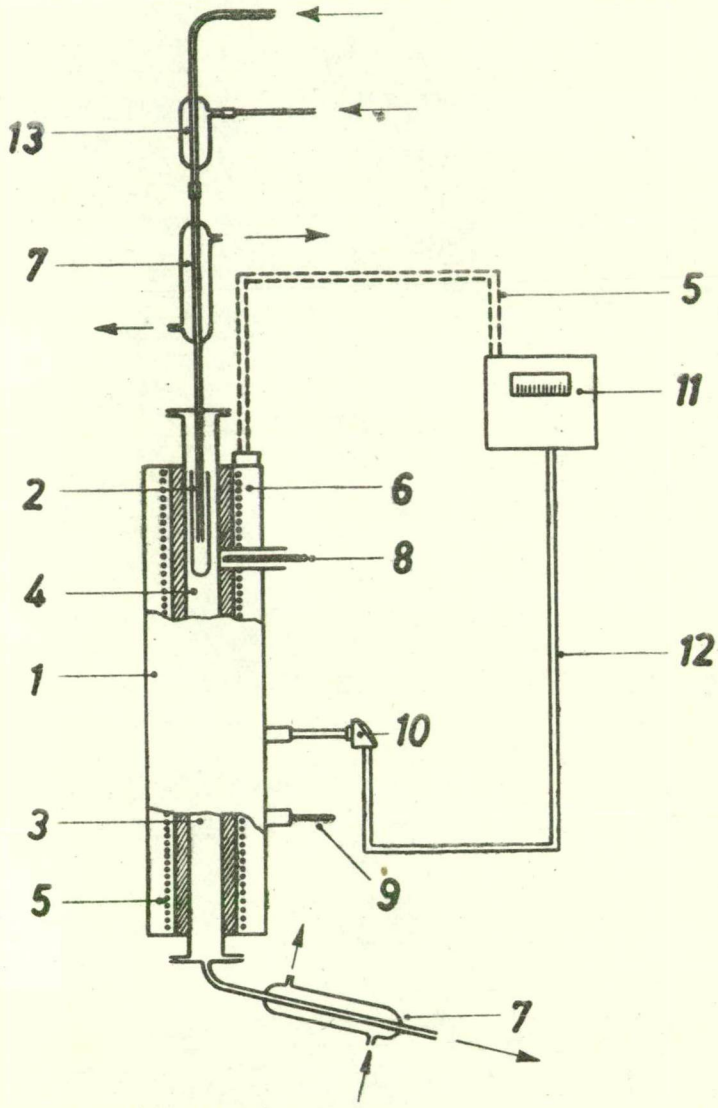


1. Dryer charged with $CaCl_2$
2. Membrane pump
3. Needle valve
4. Differential pressure gauge
5. Furfural evaporator
6. Reactor
7. Cooled receivers for the recovery of unconverted substance
8. Cooled carbon column for the recovery of furan
9. Gas meter
10. Mercury thermometers
11. Thermocouple
12. Temperature regulator

Figure 22

Glass reactor for the preparation of furan

tar layer sometimes desactivates the upper catalyst layer.To eliminate this inconvenience, the apparatus shown in Fig. 23 was designed.



1. External jacket
2. Evaporator
3. Reactor tube
4. Reactor tube
5. Heating current conduit
6. Thermal insulation
7. Liebig-condenser
8. Mercury thermometer
9. Mercury thermometer
10. Thermocouple
11. Temperature regulator
12. Thermocouple conduit
13. Furfural inlet

Figure 23

Reactor for the preparation of furan

Cold furfural and air enter the glass vessel /13/, and pass through the vertical iron Liebig-condenser /7/. Liquid flows into a large iron sleeve of test tube form /2/, which functions as an evaporator. Evaporated gases pass downwards in the cylindrical space between the reactor tube /3/ and the evaporating sleeve, form a homogenous mixture with air, arrive in a preheated condition to the catalyst, and after passing over the catalyst and being cooled in the lower Liebig condenser /7/, the isolation of furan may begin. Similar to the earlier equipment the iron reactor tube is surrounded by an aluminium block equipped with electric heat regulation.

The operation of this equipment was very satisfactory. However, when operated for a longer period, the evaporator, which could not be enlarged, was blocked. As already described in the theoretical part /Part I.C/, the method of furan production developed by us, as contrary to reductive methods described in literature, is based on oxidation which increases the reaction heat by tenfold. In the scaling up of the reactor the well known principle of tube bundles had to be applied. The reactor shown in Fig. 24, consisted of four tubes and the space between them was filled under carbon dioxide overpressure with mercury heated to its boiling point. Four and nine-tube reactors /Fig. 25/ have been put to test. The four-tube reactor operated satisfactorily even when aluminium was poured into the space between the tubes and kept with the temperature regulator /6/ at the temperature prescribed by the experimental program.

This apparatus /Fig. 25/ operated in the following way: In the evaporator /3/ heat for evaporation was supplied by a cartridge heater with internal fins. Air was introduced at the bottom of the evaporator, furfural at the top /1/. Furfural trickling down the helical plate was evaporated by and

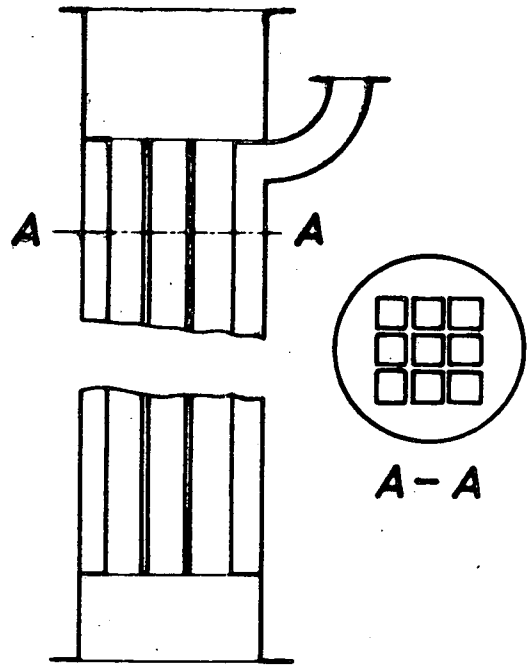


Figure 24
Reactor tube bundle

mixed with the countercurrent air flow, then passed on to the reactor tubes /4/. When a mercury was circulated in the cooling jacket, the equipment was fitted with the mercury condenser /5/. The end gases passed through cooler /7/ to separating funnel /8/ where the condensate was collected and the end gases containing furan passed on. To ensure continuous operation three iron columns packed with carbon were used, in the jackets of which steam or ice water was circulated according to requirement. The operation of the carbon and the stopcock system shown in Fig. 25 was as follows: The end

1. Liquid burette
2. Gas feeding pump with vibrator
3. Electrically heated evaporator
4. Tube bundle reactor with mercury regulated jacket
5. Mercury reflux condenser
6. Temperature regulator
7. Jacketted cooler
8. Separating funnel
9. Jacketted carbon adsorption columns
10. Receiver for condensed water
11. Gas meter
12. Cooling coil
13. Cooled receivers

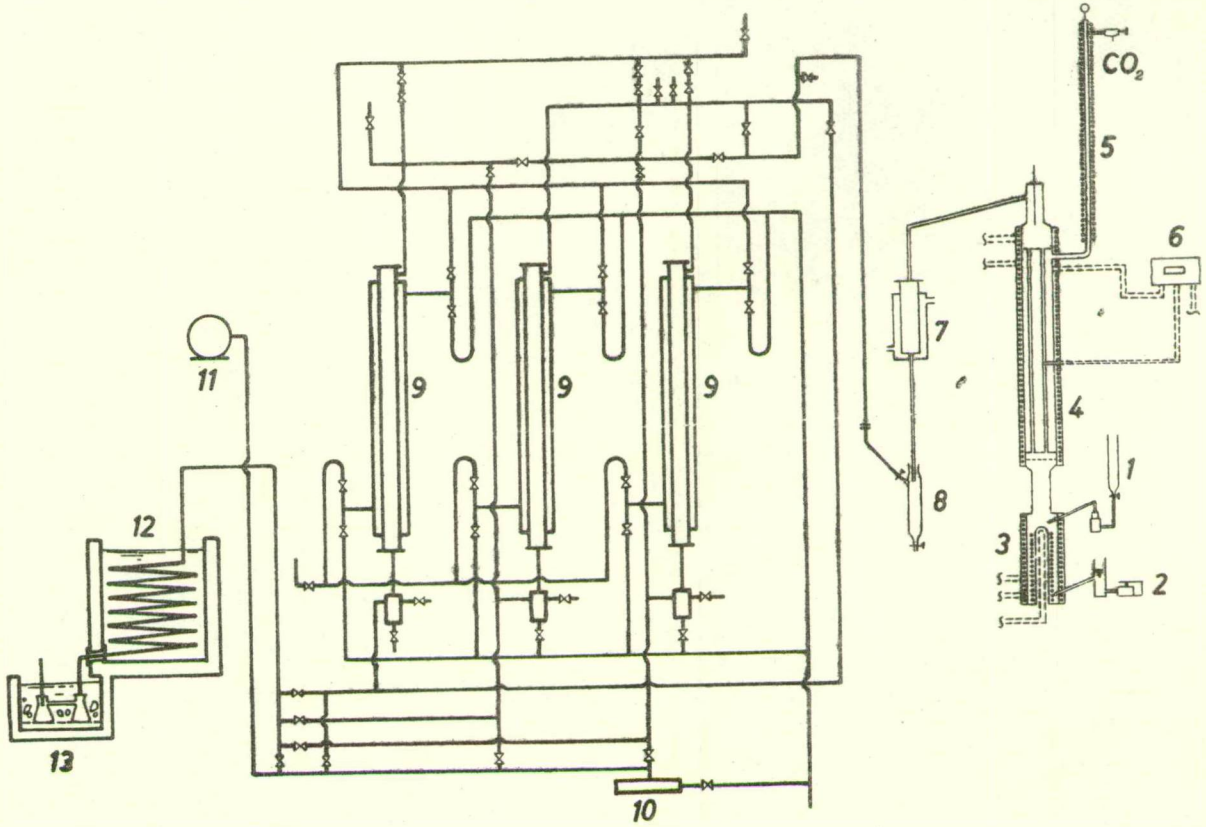


Figure 25

Mercury regulated tube-bundle reactor with continuous adsorption and desorption system

gases were introduced into the right-hand carbon column and passed then the middle, and finally the left-hand column, while furan was adsorbed by the carbon.Gas free of furan was measured with the gas meter /11/. During this process the carbon columns were cooled with tap water or with ice water. Excess water was removed through a built-in drain. Water collecting in the tubes was discarded from tank /10/. Steam was introduced at the top. When the first carbon column,i.e. that on the right side, is loaded, it is switched off, and furan is adsorbed on the middle, and finally, in the left side column.Meanwhile furan is desorbed by introducing steam into the jacket or directly over the active coal charge of the right side column. Desorbed furan passes through the cooling coil /12/ into receiver /13/. The same procedure is applied for the desorption of furan in the middle, then in the left side column, adsorption always being continued in the column at the lowest temperature, then the cycle is repeated. Since this complicated equipment divided the attention of the operator, it was considered expedient to use only a twin reactor and adsorber for production purposes. The production of furan from furfural was attempted also through other new reactions, further in apparatus suitable for a novel approach to scaling up.This work has been shortly outlined in the theoretical part /Part I,C/ and will be discussed in detail in our subsequent Operator's Manuals.

For research work, the present equipment proved to be the most suitable.

2/ Adsorption and desorption of furan

As mentioned before, the recovery of furan is essentially a capillary condensation process on active carbon. End gases are passed through the column packed with the adsorbent, and furan is bound on the surface and in the pores of the adsorbent. Adsorption activity, specific surface, and porous

structure of the adsorbent may be evaluated as described previously /See Part II, Par. B/5, 6 and C/1-6/.

The adsorption of furan on active carbon is characterized by an exceptionally high heat of adsorption. Distinction is made between two types of heats of adsorption. Integral heat of adsorption is the quantity of heat released when a specified quantity of material /e.g. 1 mole/ is adsorbed by unit surface or unit mass of the adsorbent /cal, cm^2/mole and cal/g/mole, respectively/, provided that adsorption occurs on a surface free of adsorbate. If the surface is already partly covered with adsorbate and a further quantity of da mole is adsorbed, under liberation of dq quantity of heat, the differential heat of adsorption will be

$$q = \frac{\partial q}{\partial a}$$

Differential heat of adsorption decreases with increased loading of the surface, indicating that the most active centres are saturated, and adsorption occurs in centres of decreasing activity.

Thus high heat of adsorption shows that furan is very readily adsorbed by active carbon.

Adsorption hysteresis is manifested characteristically. At the beginning of furan adsorption a "sweating" of the carbon occurs, because furan, which is very readily adsorbed, displaces water vapours always present in this case on the surface of the adsorbent. Displaced water vapour condenses on the walls of the adsorption column. This phenomenon also clearly shows the progress of the furan adsorption front and permits therefore an evaluation of the rate of adsorption and of breakthrough.

Furan is displaced /desorbed/ and recovered by the heating of the jacket or by direct blowing with steam; steam blown continuously entrains furan and gradually displaces it from the surface of the adsorbent. Under identical conditions furan is more readily adsorbed on active carbon than water vapour. This desorption requires therefore a relatively long time /with the usual dimensions of our equipment about 15 minutes/.

The adsorbent used for furan recovery was gas adsorption carbon type "Nuxit AL", made of sawdust and activated with zinc chloride. Its specific surface area is 600 to 700 m^2/g. Its total pore volume ranges 60 - 70 ml/100 g, with the following distribution of pores of various sizes:

11 Å	
11 - 20 Å:	7,5 ml/100 g
20 - 100 Å:	3,5 ml/100 g
100 - 1000 Å:	2,1 ml/100 g
1000 Å:	26,0 ml/100 g

3. The isolation of furan

On account of its high tension and low concentration it is difficult to recover furan from the end gases in a yield approximating as far as possible quantitative recovery, also this would be important both in research work and in production. The following techniques have been tested:

a/ Washers cooled with carbon dioxide and acetone connected in series were uneconomic to operate and the reading of the product quantity proved cumbersome.

b/ If, in absorption methods end gases were bubbled through solvents of furan, the furan distilled off was contaminated with the solvent used as adsorbent. This method is obviously

suitable for technical purposes, provided that the liquid used for absorption does not interfere in the utilization of furan.

c/ Undercooling or high-pressure compression of the end gases is an expensive method. This method is impracticable when working with small quantities, because of losses. Our preliminary calculations show that simultaneous application of medium pressures and medium cooling /-10 to -20°C and 10 to 20 atm/ are within the economic range for this reaction on an industrial scale.

d/ Adsorption and desorption processes on active carbon seem satisfactory both on laboratory and on industrial scale, therefore our experiments were carried out by this method on analytical, preparative and pilot plant levels. First, furan end gases were collected in receivers /Figs. 26-29/ immersed in salt and ice mixture, then transfered into the graduated part of the vessels and measured in millilitres.

In other methods, furan was adsorbed on active carbon placed in a bulb condenser, then desorbed with steam in an apparatus as shown in Figure 30. It was found disadvantageous that the temperature of the lower part of the undercooler is raised by the steam used for desorption. Therefore, steam desorption combined with IR-heating was applied in the case of the apparatus shown in Fig. 31. Furan adsorbed by active carbon in the upper bulb condenser was heated in an infrared oven, which permitted desorption with a minimum quantity of steam. The lower pre-cooler improved the economy of condensation in the undercooled part. Possibly escaping furan was trapped in the slanting bulb condenser containing cooled carbon. The discussion of the difficulties met step by step in the course of the development of our adsorption and desorption apparatus is thought to be instructive.

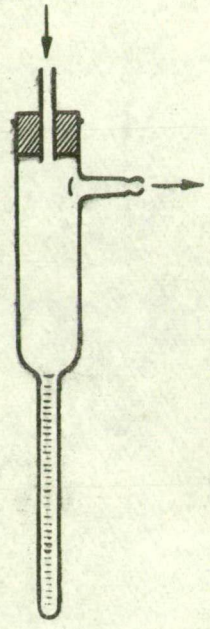


Figure 26

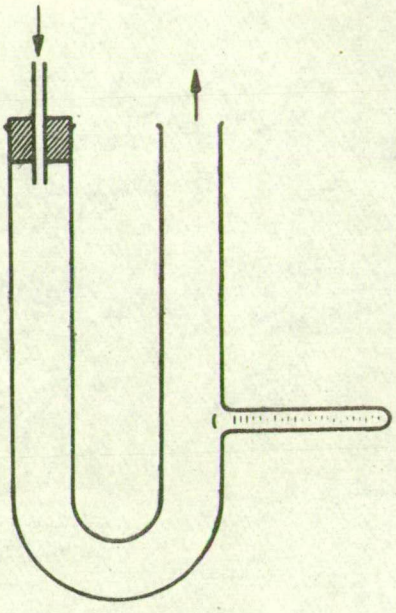


Figure 27

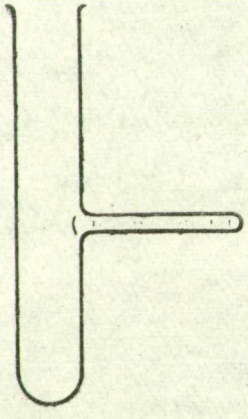


Figure 28

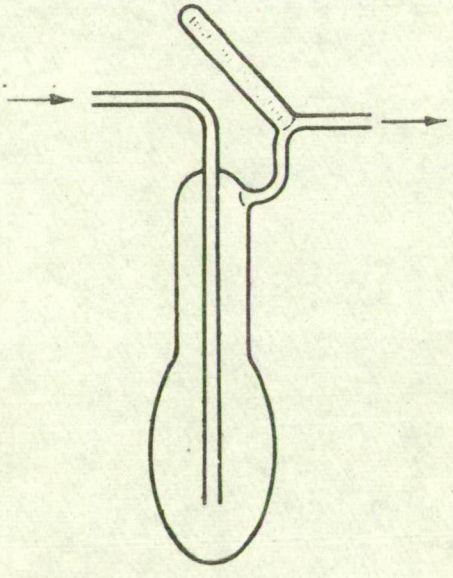
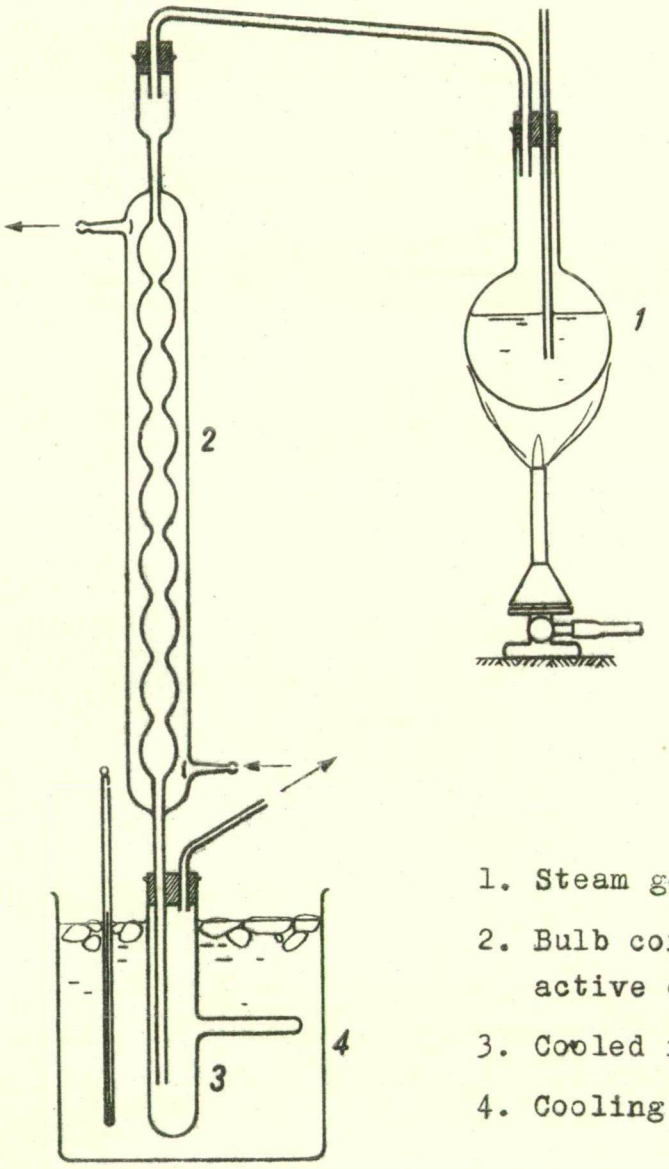


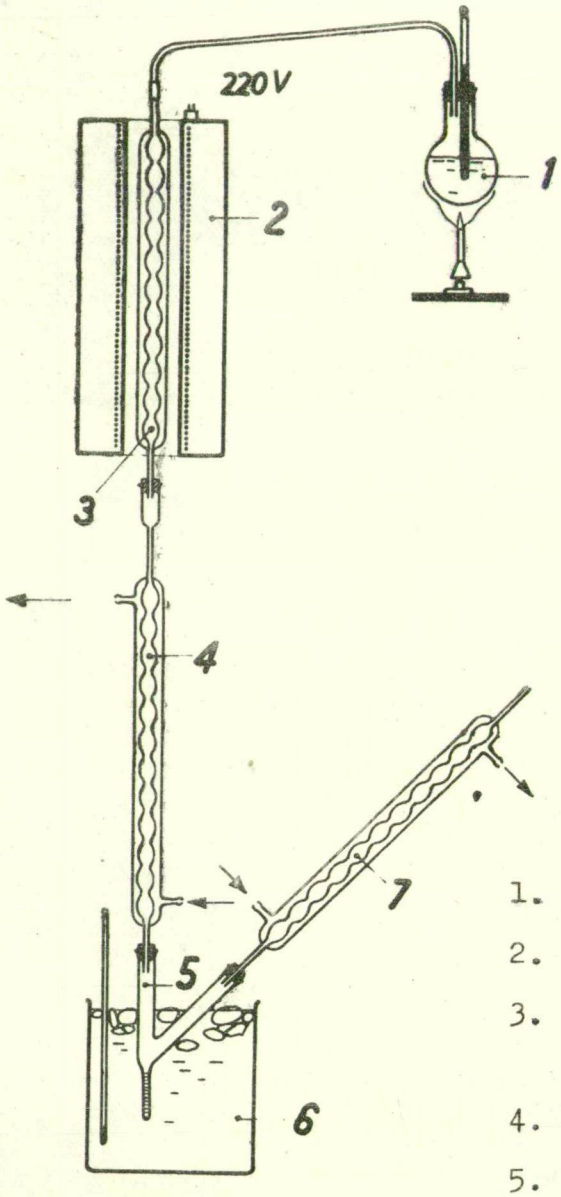
Figure 29

Cooled receivers for the recovery of furan



1. Steam generating flask
2. Bulb condenser containing active carbon
3. Cooled receivers
4. Cooling

Figure 30
Desorber



1. Steam generating flask
2. Infra-red heater
3. Bulb condenser packed with active carbon
4. Bulb condenser
5. Cooled receiver
6. Cooler
7. Bulb condenser

Figure 31

Desorber combined with infra-red heating

The apparatus illustrated in Fig. 32 has been designed to eliminate these difficulties. Steam production in the steam generator can be finely regulated by the adjustment of the flame. The carbon column above it is saturated with steam in such a way that the reflux of steam shall be limited to the centre of the upper vertical tube. Thus no water can get into the burette on the right-hand side to reduce its state of undercooling. The jacket of the undercooled burette of 50 ml volume and 0,1 ml graduations is cooled to $-20^{\circ}C$ by a circulating mixture of glycerol and water. The coolant is circulated by a gear pump built into the refrigerator. After removing the frost from the glass, the volume of the produced furan may be read with the help of an illuminating lamp to an accuracy of 0,1 ml. If ice is also present, reading is effected by first stopping the circulation of the cooling water, then raising with an infra-red lamp the temperature of the section filled with furan to about $+1^{\circ}C$. This brings about the separation of water from furan and the volume of the latter can easily be read. Under such conditions the ice, due to inclusions of furan, has a spongy structure and can be ignited. The carbon used in our experiment can adsorb about 17 per cent by weight of furan. The adsorption - desorption apparatus of the complete catalytic laboratory has been designed along the principles shown in Fig. 32.

4. Analysis of furan

The analysis of furan and its derivatives has been already fully developed. Omitting here a detailed discussion of a number of available and applied variants, we refer to the work of Z.V. Til and A.A. Ponomarev, mentioned already earlier /see Part I, Reference No. 160/, as well as to the works of M.V. Shimanskaya and V.A. Slavinskaya /see Part I, Reference No. 159/, and of A.A. Scherbakov, further to the monography of A.P. Dunlop and F.N. Peters /see Part I, References 16 and 3, respectively/.

1. Refrigerator
2. Graduated cylinder
3. Furan burette
4. Carbon column
5. Steam-generator

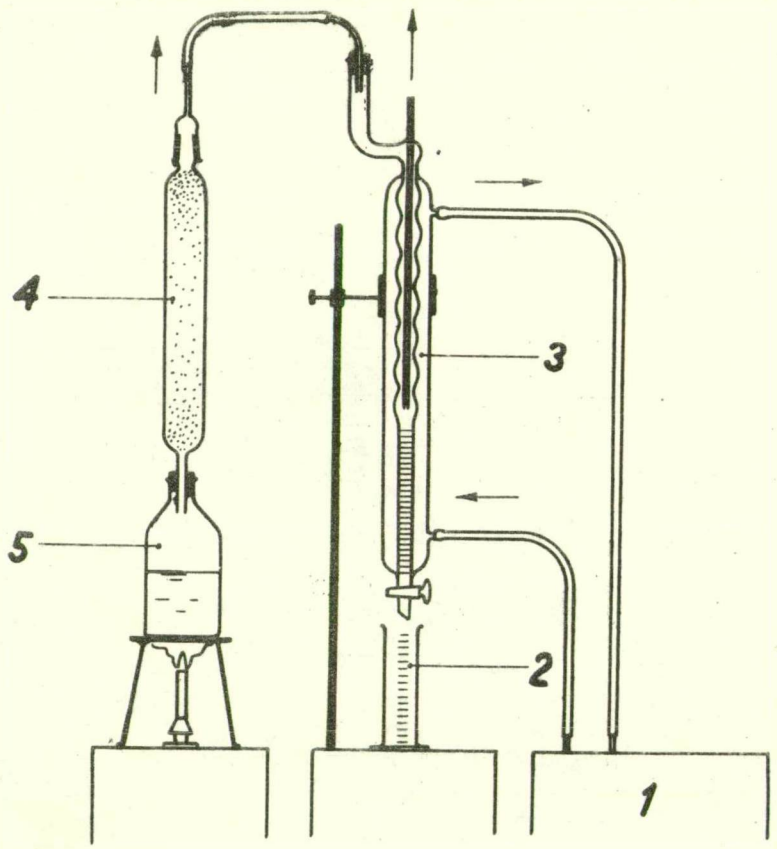


Figure 32

Steam-operated desorber with furan burette

On the basis of several considerations, the semimicropreparative apparatus and process shown in Fig. 32, equivalent to a technical analysis, was adopted, and since our aim is to find an industrial process, it was decided to consider in the calculation of yield only that quantity of furan, which can be isolated preparatively.

Specification of furan produced by us:

Colour: colourless liquid

Peroxide content: Nil.

Moisture: max. 0,15 per cent, as determined by the Karl Fischer-method

Acid content: Nil.

98 per cent of the substance distils over between 31 and 33°C. No solid distillation residue.

Specific weight: 0,933 to 0,936

$n_D^{20} = 1,4215$

Physical constants of furan are contained in Table 6, and its vapour tension curve is shown in Fig. 41.

5. Package and storage of furan and furfural

Furan boils at 31°C /for further data see Table 6/, it has a high vapour tension /see Fig. 41/. From a chemical point of view, its storage does not present problems, it decomposes and decolourates very slowly. Expediently, it will be stored at a low temperature in a container, designed to resist a few atmospheres of pressure. Under tropical conditions or in summer, the fact should be considered that ambient temperature may exceed the boiling point of furan, and thus the container has to resist a furan pressure corresponding to 45°C. At -85.6°C furan becomes solid.

Furfural is a colourless substance separating from water like oil /see Table 7/. Shaken with water, the water forms the upper, furfural the lower phase. The furfural phase con-

tains 9.1 per cent of water, while the water phase 8 per cent of furfural. On distillation, first an azeotropic mixture of furfural and water distils off, then dry furfural. Furfural can be purified by steam distillation and distillation.

After distillation the liquid turns yellow in a few minutes, brown in a few days, and when exposed to air and to light, its colour changes to black. It must be kept in coloured bottles. By adding a few thousandth part of diethylamine or pyrogallol after distillation, furfural becomes storable. In dry form it is easier preserved. Owing to its boiling point of 168°C /see Fig. 40/, it has a low vapour tension. Its transportation and storage do not require any special care. Furfural resin formed in the distillation of brown or black furfural is difficult to remove from glass. Since this problem, leading to an untimely breaking of the flask, cannot be solved satisfactorily, the equipment /iron flask/ for the distillation of furfural was designed with a removable lid.

Furfural and furan vapours in the air give rise to a transitory nausea only in case of high concentrations and on exposures for longer periods.

The inflammability of furfural may be taken to be identical with that of petroleum, and the inflammability of furan with that of ether.

6. Experiences and recommended experimental programs concerning the production of furan from furfural

Scientific and patent literature pertinent to the preparation of furan was dealt with in detail in Part I of the present volume. In the following, materials used in the process developed by us will be described. Physical and physico-chemical characteristics of materials used are summarized in Table 6.

100 per cent furfural. Commercial furfural, or in distillation, the substance of a boiling point of 160°C, distilling off after the removal of aqueous fore-runs of a boiling point of 160°C can be considered as dry, that is to say pure furfural both to industrial and experimental purposes.

Only a product readily available and easy to reproduce should be used as starting material.

90.9 per cent furfural. When furfural is shaken with water several times until the dissolution equilibrium is established, 90.9 per cent aqueous furfural is obtained as the bottom phase.

Water containing 8 per cent of furfural. When equilibrium has been attained in the preparation of 90.9 per cent furfural, the upper aqueous phase contains 8 per cent of furfural.

Air. For accurate measurements clean air shall be used. When using air, its pressure and humidity should be taken into consideration.

Nitrogen. Introduced from a nitrogen pressure flask into the reactor, and, if necessary, washed free of oxygen.

Oxygen. Introduced from an oxygen pressure flask into the reactor. It is passed through several liquid washers with the eventual intermediation of a gasometer to isolate possible back-explosions.

Carbon dioxide is introduced into the reactor from a pressure flask through an inserted pressure reducing valve.

When beginning the work, it should be kept in mind that our present knowledge in the field of catalysis permits but few predictions as regards results to be expected from the planned experiments. Thus, to make good use of time and to obtain practical results, planning must be rational.

The preparation of a catalyst is generally a difficult task, and even the reproduction of existing formulae is difficult both in the laboratory and in the plant. One of the well-known chemical factories has manufactured a vapour-phase heterogeneous catalyst for 15 years, but so far every batch had different characteristics. In spite of great efforts in the field of automation and for the attainment of reproducibility, the plant did not yet succeed in achieving completely reproducible results. Traces of contaminations in the initial materials, the very slightest variations in stirring, feed rate or temperature may result, even in case of identical chemical composition, essential changes in the crystal structure of the catalyst, affecting its use in preparative work. It is clear from the above that in the selection of a catalyst for a particular chemical reaction the number of possible variations is great. However, by using certain analogies and on the basis of economic considerations, possibilities may and ought to be reduced.

Economical aspects. Many of the factors influencing economy are often predictable. In the present case, for instance, it is advisable to start from aqueous mixtures of furfural which are easy to produce, and to use 90.9 per cent or 8 per cent furfural. Other conditions will be considered only if this furfural - water mixture, easy to produce, does not give satisfactory results.

For oxidizing purposes, instead of expensive mixtures of CO_2-O_2, first atmospheric air will be tried; recours to pure CO_2 or O_2 follows only when the first attempt has failed.

Caution should be observed also in the use of great quantities of water because, though cheap, its evaporation on an industrial scale requires much heat. In cases where much water is needed, expensive heat exchangers are required to recover this heat.

When planning our working program, we should proceed from inexpensive solutions toward expensive possibilities, as, at the beginning, the probability of the solution of the chemical problem is nearly identical in both cases. Complied, expensive or hazardous solutions should be adopted only as a necessity, when the aim cannot be attained in any other way.

With the basic materials discussed above nearly any known catalyst usually applied in oxidation reactions will be suitable. However, with regard to the afore-said, instead of using expensive metal oxides - unless as promoters - our investigations will begin with the cheapest catalysts. If our object cannot be attained in this way, expensive but well known catalysts will be tried and only when also these have failed will expensive and unknown solution be investigated.

Even for the same catalyst, several possibilities are given for the method of preparation and the selection of a carrier. On the basis of economic considerations, chemical analogies and empiric experiences, the number of experiments required may be cut down to a minimum. In the search for the best catalyst for an important chemical reaction, big factories were known to carry out as many as 10,000 tests.

Probably, catalysis and chromatography may be considered as those fields of chemistry, which are based to the highest extent on empirism, as the slightest modification in the crystal structure of the catalyst or adsorbent may result in important changes in the preparative results.

Proper and reproducible production methods often imply special details of know-how which are not always disclosed in the patents. This renders the reproduction of protected patents often very difficult, if not impossible. A person intending to reproduce as a laboratory study the work on furan-maleic anhydride or some other vapour-phase catalytic process described in literature or in patents, will meet great

difficulties. On the other hand, Nielsen's papers on the production of maleic anhydride and the publications of the Lithuanian Research Institute for Catalysts /see Part I, B/ deserve special mention as perfectly reproducible works.

In describing our series of experiments we wish to put examples of reproducible results at the disposal of the reader. When selecting the catalysts to be used in the present work we have paid great attention also to the fact that they should not be sensitive to contaminations or poisons: a consideration of great practical importance as regards reproducibility.

All specified feed rates of the initial materials can be reproduced, both individually and in relation to one another. A sudden sharp change may occur, depending on whether air is fed to furfural above or below the stoichiometric quantity as the excess air increases the risk of resinification. Too high temperatures cause burning, smoke formation, cracking, poor conversion; while conditions deviating from optimum result in undesirable by-products. When the temperature drops to or below 250°C and the quantity of air is increased ten times the stoichiometric quantity or more, maleic anhydride is obtained from furfural instead of furan.

When starting up our reactor, it must be operated for at least two hours to attain thermodynamical and thermochemical equilibria, and only after this is a quantitative evaluation of the continuously recorded data to be recommended. Experiments running for at least ten hours should be evaluated, because otherwise shorter periods furnish irrealistic results. Chemical parameters must be measured with the highest possible accuracy. Precise work, an accepted rule in preparative chemistry, is even more important in vapour-phase heterogeneous catalytic methods.

The leading principle in designing the present vapour-phase heterogeneous catalytic laboratory was to ensure an accurate safe operation, as this equipment may be considered as a complex evaluating instrument of the given chemical reaction, permitting the measurement of the various reaction parameters. A further requirement is the suitability of our equipment for the development of an industrial plant on the principle of stepwise scale up, under simultaneous application of computation and empirism.

The parameters specified in the experimental program should be strictly observed in carrying out the experiments. The importance of this point will be clear if the fact is considered that at a certain value of space velocity, temperature, pressure, etc. the change of one of the parameters implies that of the others. A rise in temperature changes space velocity, pressure, concentration, and thus the rate, and possibly the direction, of the reaction. Naturally, distinction should be made between less sensitive and hypersensitive reactions. Dehydration on aluminium oxide, for instance, is a reaction of moderate sensitivity. Such reactions, however, are very rare in the field of catalysis.

In the production of furan from furfural a total absence of water is unnecessary, because water is always formed in the reaction. When during the operation perfectly dry air contacts dry furfural in the reactor, also water is formed, due to instantaneous partial over-combustion.

Experiments are carried out in general by using the cheapest material of construction for the reactor walls. One of the task is to test various materials of construction with the same catalyst and under identical conditions of reaction, - reactor space and at optimum yield in order to select the most advantageous material of construction for the walls from the point of view of future operational costs. Neither

is it a matter to be neglected whether the desired result is obtained with a catalyst of analytical purity, chemical purity or technical grade.

Wall effects are considerable and often cause disturbances when the catalyst space is too small, as in this case the surface of the wall as compared to catalyst space cannot be neglected.

As mentioned already in the theoretical part, oxidative decarboxylation instead of decarbonylation is used in our process for the production of furan from furfural with a consequent increase of the reaction heat to its tenfold. This drawback can be compensated only if advantages of other favourable characteristics outweigh disadvantages involved by high heat of reaction.

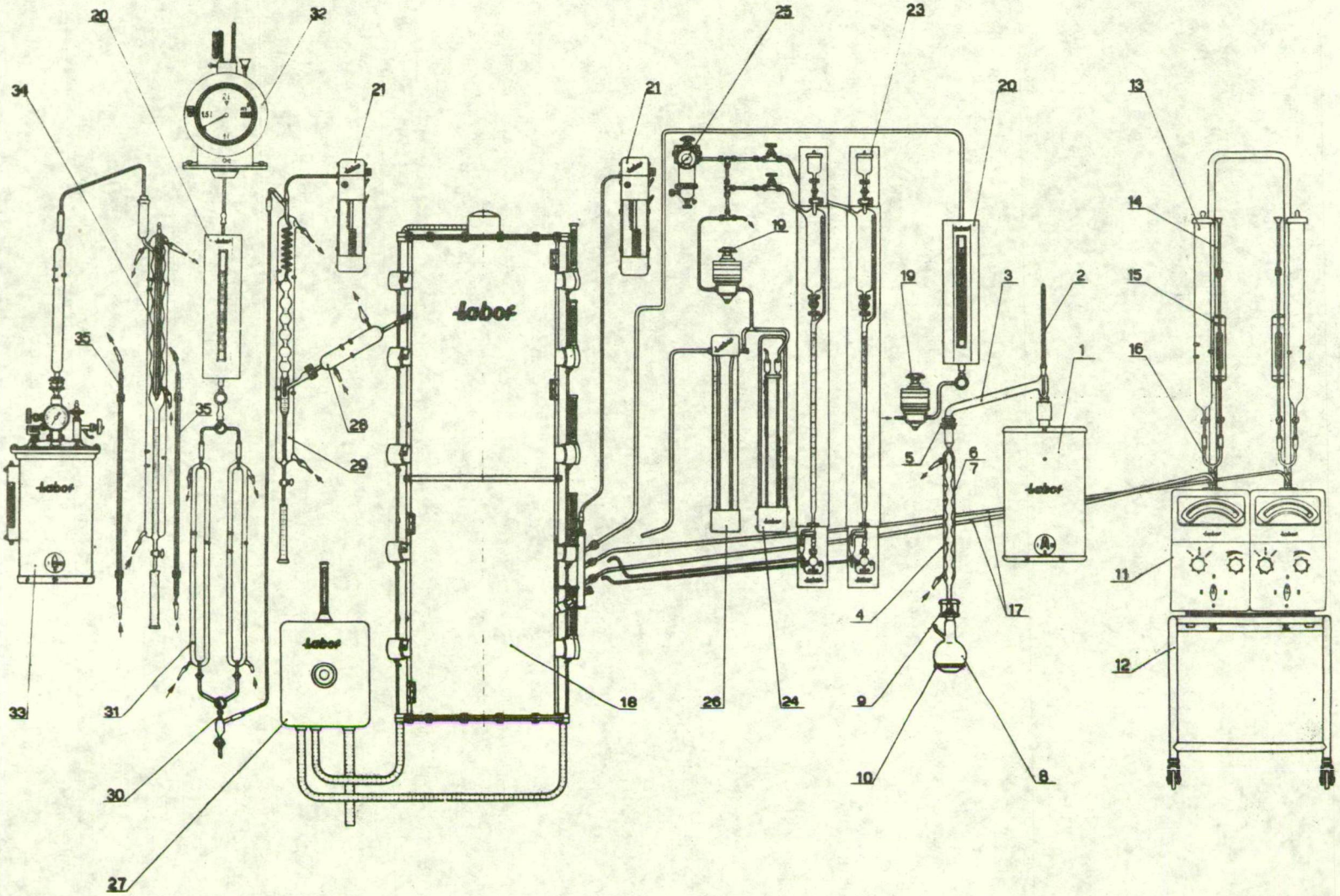
7. Description of the apparatus

Accessories shown in the flow sheet, Fig. 33 /for details see Volume I/2, "Technical Description"/, are fastened on the chemical mounting panel. The chemical mounting panel supplies communal services /hot and cold water, steam, gas, compressed air, vacuum, drainage, gas exhaustor, power etc./ to the complex equipment. The chemical reaction takes place in the reactor, the temperature and heating of which are controlled by the instruments and switches arranged on the electrical mounting panel. Communal services may be connected up to local mains or may be supplied partly or entirely by the Enterprise METRIMPEX together with the complete catalytic laboratory. Communal services, which can be furnished at present are: compressor with automatic switching on and off within an adjustable pressure range; and a combined refrigerating machine. The latter performs up to 25°C the tasks of all those laboratory refrigerators which, as various special task refrigerators, are available on the world market. De-

1. Steel distillation flask
2. Ground glass distillation headpiece
3. Thermometer, 20 - 200°C
4. Bulb condenser
5. Spherical ground joint clamp
6. Three-finger flask-holder
7. Double clamp nut
8. Receiver
9. Ground joint holder
10. Holding ring
11. Feed pump
12. Pipe trundle stand
13. Separating funnels
14. Measuring burettes
15. Lighting fitting
16. Y-shaped glass connection tubes
17. Capillary conduct
18. Reactor
19. Pneumatic stabilized reducer
20. Rotameter
21. Phototransistorized pressure gauge
22. Pneumatic reductor
23. Fine feeders
24. Differential pressure gauge
25. Glass T-tube
26. U-tube manometer
27. Thermostat for thermoelements
28. Metal Liebig-condenser
29. Coil and bulb condenser
30. Distributing cock-system with water pockets
31. Carbon columns
32. Gas meter
33. Evaporator
34. Combined cooler
35. Cooling walls

Figure 33

Flow sheet 1 of the "Complete catalytic laboratory"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tailed description of the single units of equipment in respect of machinery and instrumentation is given in Volume II of "Operator's Manual".

The heating up of the reactor takes 1.5 to 2 hours, therefore the apparatus should be switched on to allow the warming up before the experiment. This is carried out as follows: The main push button of the electric mounting panel is pushed in, this switches on the three red pilot lamps which indicate the presence of the three phases, and the apparatus is put under voltage. Next, the button marked "Reactor", is pushed in, which switches on the red pilot lamp on the top part of the switchbox, and current flows to the switches of the reactor.

Corresponding to the five sectors of the reactor, two switches are provided for each of the sectors denoted by Roman numbers. By turning the left switch of each pair and setting the right one to automatic operation, the warming up of the corresponding heating sector of the reactor begins. By turning on also the further two switches of the switch box, the red pilot lamp indicating the voltage of 220 V and the green pilot lamp indicating the voltage of 24 V light up on the chemical mounting panel.

Now the electric equipment on the chemical mounting panel may be switched on; thus the distillation still, the evaporator, the phototransistorized pressure indicator and the lamps facilitating readings, which are arranged behind the rotameter and the glass tubes of the burettes. The electric mounting panel has five scales marked with Roman numbers identical with those on the switches on the desk, indicating the electric and thermic characteristics of the single reactor sectors.

Electric current arrives through a toroid transformer, and is conducted through a voltmeter and an ammeter to the heat-

ing cartridges of the reactor. Circuit is interrupted or closed, as required, by a phototransistorized temperature controller. In order to adjust this controller to the desired temperature, the red pointer is adjusted by the aluminium wheel on the upper right side to indicate as reactor wall temperature the temperature prescribed by the experimental schedule. This temperature is measured by bent nitrogen-overpressure mercury thermometers arranged on the right side of the reactor and the measured values are recorded by a six-colour multi-point recorder mounted on the right side of the switchbox. After the setting of the temperature, the heating current is switched with the help of the toroid transformer to maximum intensity checked by instruments. Simultaneously, the control mechanism of the apparatus is switched on with the switch below the punctograph. On attaining the desired temperature the phototransistorized temperature controller maintains the reactor at this set value.

Should the temperature controller fail, the switches of the reactor sectors are changed over from automatic to manual control position and, checking the temperature on the mercury thermometers, the intensity of the heating current is regulated with the toroid transformer so as to keep the temperature at the desired value. In order to lengthen the service life of the instruments, this can be done also in automatic position /in this case, the instrument switches on current of lower intensity/.

When the reactor has warmed up, also the temperature prevailing along the reactor can be read on the millivoltmeter calibrated to centigrades, which is located on the upper left corner of the switchbox. The values of temperature along the axis of each sector are indicated by lamps on the mimic reactor scheme below the instrument. These lamps can be switched on with the central buttons 0, II, III and IV, respectively, on the left side of the desk. The plug socket holder for 220 V on the right side of the desk permits the use of a

desk lamp or a mounting lamp. Current for the synchronous, electric clock on the electric mounting panel is supplied from the lighting. The chief function of this clock is to give relative time values for the records of the chemical work. The time while the reactor is warming up, may be used to prepare pure freshly distilled furfural for the reaction in the apparatus denoted by 1 - 10 on the flow sheet. Furfural is poured into the metal still and distilled off according to the general rules of operations in preparative laboratories of organic chemistry, starting with switch position III, then changing over to positions II and I. If, nevertheless, distillation proceeds too vehemently, the current is cut off, and switched on only periodically to position I. Heating with a toroid transformer, equipped with volt- and amperemeter is more advantageous. The freshly distilled furfural is poured into the feeding vessel of the fine feeder burette /23/, the compressor is switched on, and after the opening of the air-cock, an overpressure of 2 atm is applied with the stabilized gas reducer /22/ to the surface of the furfural. The pressure is checked with pressure gauge /25/. Next, the fine feeder burette is filled up, and the desired feed rate is adjusted with the needle valve. Simultaneously, the prescribed quantity of air is fed with the help of the stabilized reducer /19/ and the differential pressure gauge /24/ into the reactor.

If required by the experimental program, another liquid component may be fed from the other fine feeder. Meanwhile, the cooling water circulation of the Liebig /28/ and the combined /29/ condenser is started. The phototransistorized pressure indicators /21/ are switched into pressure position /they may be switched also into vacuum position/, and the light signal is set to the permissible pressure limit. If this pressure is overstepped by the system, for example in case of clogging caused by carbon deposition, audible alarm and light signal warn the operator.

The introduced liquids evaporate in sector I of the reactor, mix with the air feed and arrive preheated into catalyst zones II, III. and IV of the reactor. Here, reaction proceeds on the contact surface, and vapours flow through the precooling zone V into the Liebig-condenser /28/.

Unconverted material condenses in the cooler, and, after the reading of its volume, on the burette of the combined coil--and-ball condenser /29/ is removed through the draincock of the condenser for purification by distillation for further experiments. Uncondensed vapours and gases flow first through the bulbs, then through the coil of the cooler to the distribution head, and from here, at corresponding stopcock positions, into the carbon column /31/. Furan is adsorbed by the carbon and the other gases flow through the rotameter /20/ and through the gas meter /32/ to the exhaust hood.

Care should be taken that the outlet rubber tube of the gas meter shall not be too near to the exhaust hood, because the gas meter is devised for a pressure of a few centimeters of water column and data may get falsified by the sucction effect.

After the saturation of the carbon column, stopcocks are turned over the twin column, the loaded column is removed and transferred to the top of the evaporator /33/.

With the help of the refrigerator, glycerol-water mixture at $-25^{\circ}C$ is circulated in the undercooled burette /34/ and the furan-burette is cooled to -20 to $-25^{\circ}C$. Simultaneously, the water circulation of the water cooling wall /35/, protected by chromium coated surface against heat radiation, is started. The object of this cooling wall is to protect both sides of the furan-burette cooled to $-20^{\circ}C$ against heat radiation from the reactor and the evaporator, respectively. Before cooling, expediently the furan-burette will be wiped off

with cottonwool moistened with glycerol, to eliminate frosting, which renders readings difficult. After cooling, the switch of the evaporator /33/ is turned into position III until steam is evolved. Next, the evaporator is switched over to position II or I, according to requirement, and the choke and blow off needle valves are adjusted so that the upper limit of steam condensation, manually and visually perceptible, shall be situated at the middle of the vertical part of the glass tube above the carbon column.

Desorbed furan is collected in the lower part of the burette and its volume is read on the burette. In our experiments, this determined value represents also a result of technical analysis. Collected furan is stored in the part at $-20^{\circ}C$ of the refrigerator. Cooling water is discharged into the next drain.

For the feeding of greater volumes of liquid reactant, a motor pump is used as follows: Furfural is poured into the funnel /13/, fitted with a lid, and meniscus levels are equalized by opening the stopcock of the funnel and that of the burette /14/. The desaeration needle valve at the back of the pump is opened, and maintained in this position until liquid free of air bubbles departs. Next, both the needle valve and the stopcock of burette /14/ is closed, the motor is started, the desired step and stroke length is adjusted with the corresponding control knobs and the drop per minute of the meniscus in the burette is determined. This value gives the volume of the liquid fed in unit time. After the determination of this value, the stopcock of the burette is closed and that of the separating funnel opened. With the twin pump, several hundred millilitres of furfural and water or other two liquids can be fed in an hour.

The differential manometer is unsuitable for the feeding in of greater volumes of air. For this purpose a rotameter se-

ries is used, the specification of which, similarly to that of other units shown in the flow sheet, is given in detail in Volume I/2.

Gas flow through the rotameter at adequate constant pressure, may be regulated with a needle valve until the float of the rotameter attains the desired value.

Stabilizing reducers are operated as follows: The outlet stopcock of the compressor is opened, and by turning the knob of the reducer to the right side, outlet pressure is increased to the desired value. After use and before closing the stopcock, the knob is returned to its original position by turning in the opposite direction. If the knob is not turned back, a sudden increase in pressure may result in the bursting of the membrane. The fine feeder is refilled from the storage vessel arranged on top of the burette and separated from the latter by a stopcock. The pressure equalizing tube permits also a refilling under pressure of the burette from the storing vessel through the tap.

8. Description of an experimental run

For the description of this experimental run given as an example, we purposely selected parameters which do not represent either most advantageous or most disadvantageous conditions. It was assumed that four of the control instruments had broken down, and the apparatus had to be switched over to manual control. The reactor was charged with PbO catalyst on Al_2O_3 carrier. /The formula of the catalyst is given in Part III, Paragraph E/6./ The grain size of catalyst averaged 2 - 4 mm and it was isodimensional. The volume of the catalyst space had to be determined to permit the selection of feed rate and space velocity.

$$V = /R^2 - r^2/ \cdot 3,14 \cdot h \cdot q$$

where: R - the radius of the reactor = 1,6 cm
r - the radius of the thermometer in the axis of the reactor = 0,3 cm
h - the length of the catalyst space = 66,5 cm
q - space utilization factor = about 0,7
V - /2,56 - 0,09/ . 3,14 . 66,5 . 0,7 = 360 ml

Feeding of air at a rate of 25 - 30 litres per hour was commenced in the heating up period of the reactor when it has attained a temperature of 200°C. One hour after the attainment of the operational temperature feeding of furfural in a quantity corresponding to the experimental program was started. Preliminary investigations showed this time to be sufficient for the saturation of catalyst with furfural. Measurements and the introduction of steam into the carbon columns was begun only afterwards.

The enclosed test record /see Fig.34/ contains the numerical data on this experimental run, the most important of which, essential for evaluation, may be summarized as follows:

Temperature of the reactor wall during operation as read on the enclosed diagram registered by the punctograph was 265°C.

Feed rate of furfural: 26,2 ml/hr.

Feed rate of air: 30 lit./hr.

Total volume of introduced furfural: 153 ml; out of this 81,3 ml was converted; from the latter 0,6 ml was over-oxidized, and thus: amount of recovered furfural 71,7 ml.

Total time of experiment: 350 minutes.

Total air feed: 175 litres.

No	Time			Feeding								Pressure								Gas meter		Condensate burette			Feeding rate			Space velocity			O_2 + furf.	Contact time	Material balance	Conversion	Yield
				Fine feeder				Pump				Rota		Differencial pressure gauge			Hg manometer																		
												Feeder	End gas	left	right	total	left	right	total	Valuel	End gas	Total	Furf.	Differ.	Furf.	Water	Air	Furf.	Water	Air					
	Month	hour	min	ml	diff	ml	diff	1000	25	1000	25																							
1	Aug.29	13	07	48	0									45	15	60	93	102	195	25,8	0	0	0	0										
2		14	02	23	25									45	15	60	93	102	195	43,2	17,4	11	11	0										
3		14	51	2	21									45	15	60	93	102	195	58,8	15,6	26	25,5	0,5										
4	Aug.30	11	47	50	0									45	15	60	93	102	195	21,5	0	0	0	0										
5		13	39	2	48									45	15	60	93	102	195	81,4	59,9	19	18	1										
6		13	43	50	0									45	15	60	93	102	195	83,7	0	0	0	0										
7		14	17	34	16									45	15	60	93	102	195	01,8	18,1	6	5,7	0,3										
8	Aug.31	9	58	46	0									45	15	60	93	102	195	19,1	0	0	0	0										
9		11	38	3	43	-	-	-	-	-	-	-	-	45	15	60	93	102	195	69,3	50,2	23	22,5	0,5	26,2	-	30 1	0,73	-		0,84	13,7		52,2	18,8
10				153																161,2			71,7	2,3										

	Phototransistorized temperature controller															Themocouple reactor wall					Hg thermometer reactor wall					Centre of reactor			Refrigeretor		Furan burette	
	I			II			III			IV			V																			
	°C	V	A	°C	V	A	°C	V	A	°C	V	A	°C	V	A	I	II	III	IV	V	I	II	III	IV	V	II	III	IV	I	II	Furan	Water
1	231	114	1,8	219	113	1,5	234	107	1,5	225	109	0,5	213	122	1,2	248	266	269	258	270	195	226	222	222	215	233	238	238				
2	231	113	1,8	219	112	1,5	237	107	1,5	229	109	0,5	213	121	1,2	246	265	269	258	268	195	226	223	223	215	232	238	237				
3	231	113	1,8	219	112	1,5	237	107	1,5	225	109	0,5	213	121	1,2	246	265	270	258	268	195	226	223	223	215	232	238	239				
4	229	115	1,8	219	113	1,5	233	104	1,5	225	109	0,5	212	121	1,2	245	266	271	259	271	193	226	219	220	215	232	234	235				
5	225	116	1,8	229	115	1,5	243	107	1,5	229	109	0,5	219	122	1,2	248	270	271	265	272	200	235	227	227	220	235	240	240				
6	228	116	1,8	229	115	1,5	243	107	1,5	229	109	0,5	219	122	1,2	248	270	271	265	272	200	235	227	227	220	235	240	240				
7	227	116	1,8	229	115	1,5	243	107	1,5	229	109	0,5	219	122	1,2	248	270	271	265	272	200	235	227	227	220	235	240	240				
8	231	115	1,8	229	114	1,5	242	106	1,5	232	108	0,5	229	122	1,2	250	271	270	268	273	205	230	225	227	226	240	242	241				
9	235	115	1,8	223	114	1,5	238	105	1,5	228	108	0,5	215	121	1,2	249	270	270	267	270	195	230	223	222	220	232	239	240	-20	0	25	-
10																																

In the enclosed test record all measurable data are entered, measurements were made at arbitrary times.

Calculations:

$$A = \frac{\text{Furfural converted, moles}}{\text{Furfural introduced, moles}} = \frac{0,984}{1,851} = 0,522$$

$$A\% = A \cdot 100 = 0,522 \cdot 100 = \underline{52,2 \text{ per cent}}$$

$$T = \frac{\text{Furan formed, moles}}{\text{Furfural introduced, moles}} = \frac{0,344}{1,851} = 1,188$$

$$T\% = T \cdot 100 = 0,188 \cdot 100 = \underline{18,8 \text{ per cent}}$$

$$K = \frac{\text{Furan formed, moles}}{\text{Furfural converted, moles}} = \frac{0,344}{0,984} = 0.354$$

$$K\% = K \cdot 100 = 0,354 \cdot 100 = \underline{35,4 \text{ per cent}}$$

$$T_e = \frac{\text{Feed rate of furfural, ml/h}}{\text{Catalyst volume, ml}} = \frac{26,2}{360} = 0,073$$

$$I = \frac{\text{Catalyst volume, ml}}{\text{Feed rate of furfural, ml/h}} = 13,7$$

$$\text{Feed rate} = \frac{\text{Material introduced, ml}}{\text{Time, min.}} = \frac{153,60}{350} = 26,2 \text{ ml/h}$$

9. Series of experiments on the furfural-furan conversion

a/ Catalyst : V_2O_5 and Al_2O_3 1:1

Molar ratio oxygen/furfural: 2:1

Volume of catalyst : 278 ml /V_2O_5/

Te /space velocity/ : 0,05 sec^{-1}

I /contact time/ : 13,0 sec

Temperature : a_1/ = 250°C
a_2/ = 300°C
a_3/ = 350°C
a_4/ = 400°C

For abbreviations see Paragraph 8.

a_1/ Furan yield was so low during the reaction that reactions proceeding at 250°C could not be evaluated $\bar{A}$ = 22.6%

a_2/	A = 30,8% ;	A = 31,2% ;	A = 30,4%	$\bar{A}$ = 30,8%
	T = 0,56% ;	T = 0,50% ;	T = 0,60%	$\bar{T}$ = 0,55%
	K = 1,83% ;	K = 1,60% ;	K = 1,98%	$\bar{K}$ = 1,80%
a_3/	A = 57,0% ;	A = 54,0% ;	A = 53,5%	$\bar{A}$ = 54,8%
	T = 15,0% ;	T = 16,0% ;	T = 14,8%	$\bar{T}$ = 15,2%
	K = 26,5% ;	K = 29,0% ;	K = 26,8%	$\bar{K}$ = 27,4%
a_4/	A = 70,0% ;	A = 66,5% ;	A = 68,0%	$\bar{A}$ = 68,1%
	T = 3,0% ;	T = 1,9% ;	T = 2,5%	$\bar{T}$ = 2,4%
	K = 4,2% ;	K = 2,8% ;	K = 3,6%	$\bar{K}$ = 3,5%

	°C	A/%/	T/%/	K/%/
a_1	250	22,6	-	-
a_2	300	30,8	0,25	1,8
a_3	350	54,8	15,2	27,4
a_4	400	68,1	2,4	3,5

b/ Catalyst : PbO on Al_2O_3 carrier

Molar ratio oxygen/furfural: 1 : 1

Volume of catalyst : 360 ml

Te /space velocity/ : 0,072 sec^{-1}

I /contact time/ : 13,8 sec

Temperature: : b_1/ = 225°C

b_2/ = 250°C

b_3/ = 280°C

b_4/ = 300°C

b_1/	A = 52,2% ;	A = 49,5% ;	A = 54,3%	$\bar{A}$ = 52,0%
	T = 13,2% ;	T = 11,9% ;	T = 17,8%	$\bar{T}$ = 14,3%
	K = 25,2% ;	K = 24,4% ;	K = 32,7%	$\bar{K}$ = 27,4%
b_2/	A = 58,0% ;	A = 55,8% ;	A = 60,1%	$\bar{A}$ = 57,7%
	T = 21,0% ;	T = 20,2% ;	T = 21,8%	$\bar{T}$ = 21,0%
	K = 35,6% ;	K = 34,7% ;	K = 36,3%	$\bar{K}$ = 35,5%
b_3/	A = 69,4% ;	A = 72,5% ;	A = 73,1%	$\bar{A}$ = 71,7%
	T = 18,7% ;	T = 17,9% ;	T = 19,0%	$\bar{T}$ = 18,3%
	K = 26,9% ;	K = 27,4% ;	K = 25,9%	$\bar{K}$ = 35,5%
b_4/	A = 86,0% ;	A = 84,1% ;	A = 83,1%	$\bar{A}$ = 84,4%
	T = 19,0% ;	T = 18,5% ;	T = 18,1%	$\bar{T}$ = 18,1%
	K = 22,3% ;	K = 21,9% ;	K = 21,7%	$\bar{K}$ = 21,7%

	°C	A/%/	T/%/	K/%/
b_1	225	52,2	14,3	27,4
b_2	250	57,7	21,0	35,5
b_3	280	71,1	18,3	26,7
b_4	300	84,4	18,1	21,7

c/ Catalyst : PbO on aluminium grits

Molar ratio oxygen/furfural: 1 : 0,8

Volume of catalyst : 447 ml

Te /space velocity/ : 0,057 sec^{-1}

I /contact time/ : 17,6 sec

Temperature : c_1/ = 225°C

c_2/ = 250°C

c_3/ = 275°C
c_4/ = 285°C

c_1/	A = 89,6% ;	A = 89,9% ;	A = 90,2%	$\bar{A}$ = 89,9%
	T = 17,9% ;	T = 16,1% ;	T = 19,8%	$\bar{T}$ = 17,9%
	K = 20,1% ;	K = 17,9% ;	K = 22,6%	$\bar{K}$ = 20,1%
c_2/	A = 87,3% ;	A = 83,5% ;	A = 91,2%	$\bar{A}$ = 87,3%
	T = 19,0% ;	T = 18,8% ;	T = 19,3%	$\bar{T}$ = 19,0%
	K = 21,8% ;	K = 22,5% ;	K = 21,1%	$\bar{K}$ = 21,8%
c_3/	A = 98,0% ;	A = 94,3% ;	A = 90,3%	$\bar{A}$ = 94,3%
	T = 30,6% ;	T = 29,0% ;	T = 27,4%	$\bar{T}$ = 29,0%
	K = 31,5% ;	K = 30,6% ;	K = 29,7%	$\bar{K}$ = 30,6%
c_4/	A = 86,5% ;	A = 85,4% ;	A = 87,7%	$\bar{A}$ = 86,5%
	T = 11,2% ;	T = 12,3% ;	T = 10,1%	$\bar{T}$ = 11,2%
	K = 14,5% ;	K = 14,4% ;	K = 14,7%	$\bar{K}$ = 14,5%

	°C	A/%/	T/%/	K/%/
c_1	225	89,9	17,9	20,1
c_2	250	87,3	19,0	21,8
c_3	275	94,3	29,0	30,6
c_4	285	87,7	11,2	14,5

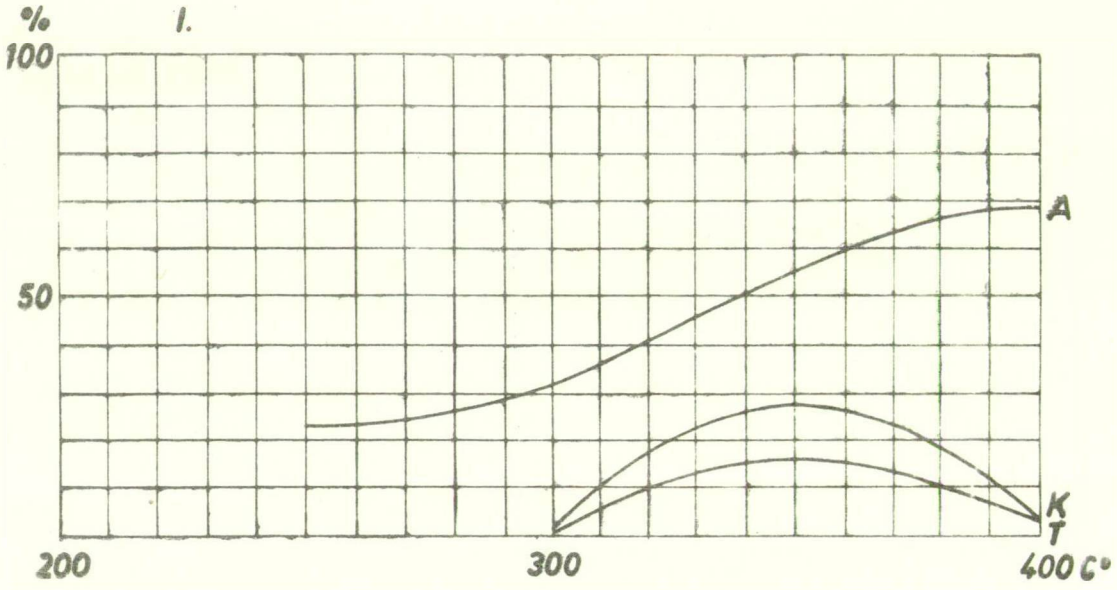

Figure 35

Dependence of the evaluation factors of furfural-furan conversion on temperature /V_2O_5 catalyst/

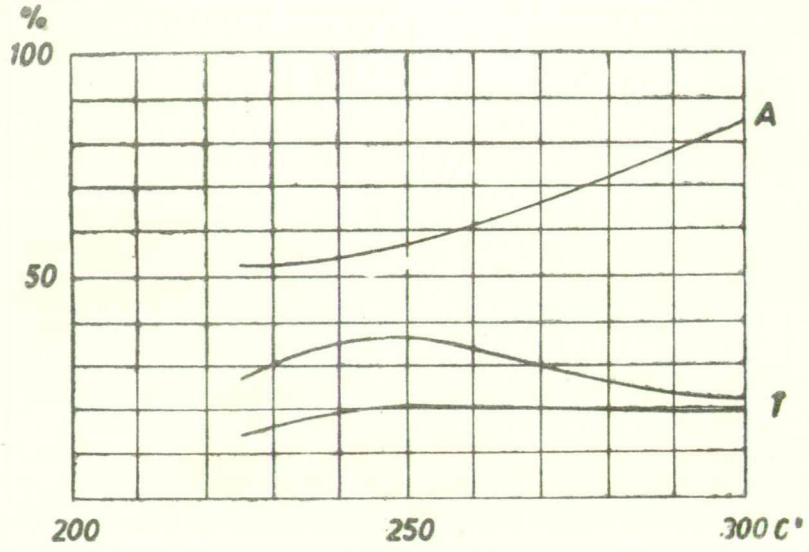

Figure 36

Dependence of the evaluation factors of furfural-furan conversion on temperature /Pb catalyst on Al_2O_3/

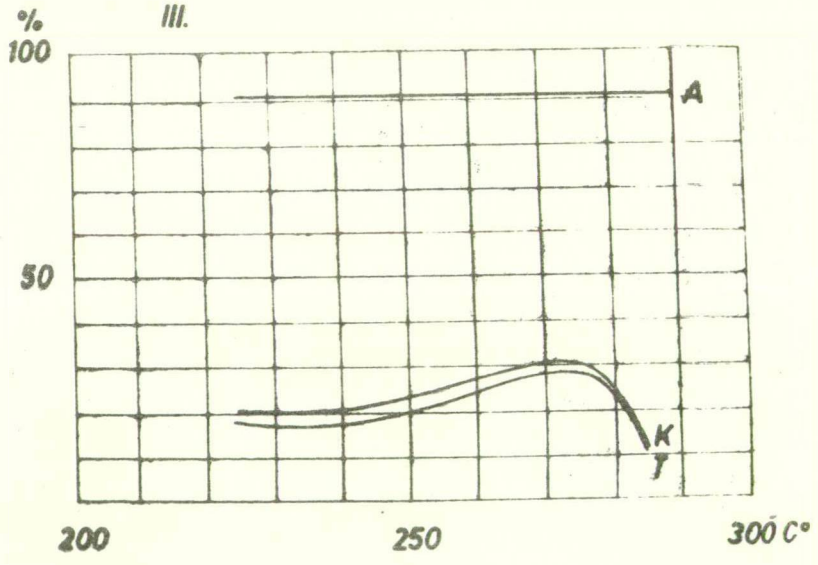

Figure 37

Dependence of the evaluation factors of furfural-furan conversion on temperature /PbO catalyst on Al-grit/

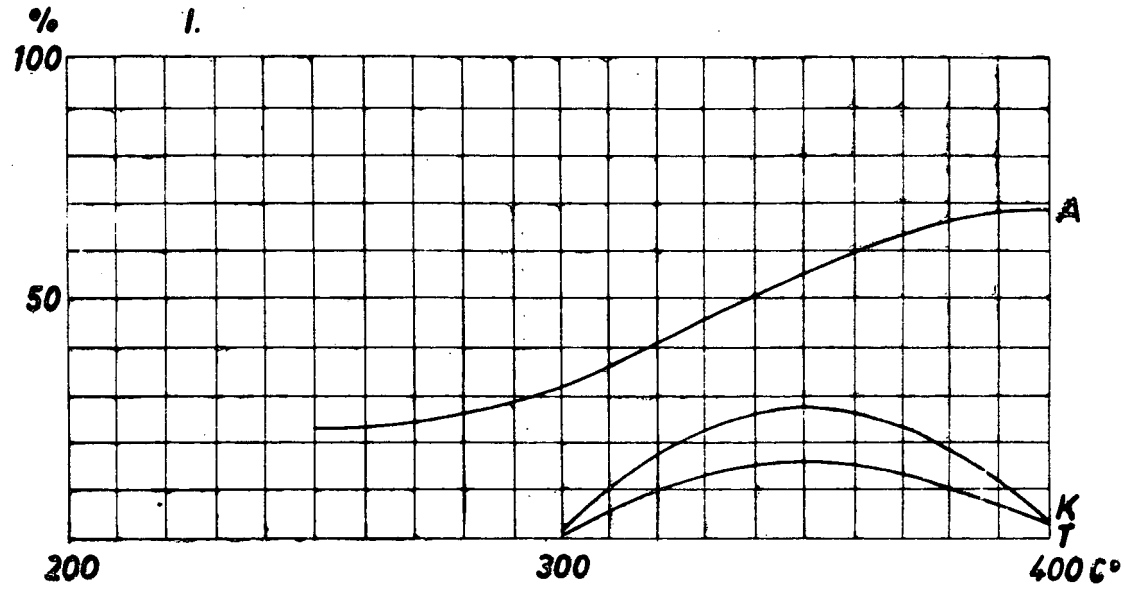

Figure 35

Dependence of the evaluation factors of furfural-furan conversion on temperature /V_2O_5 catalyst/

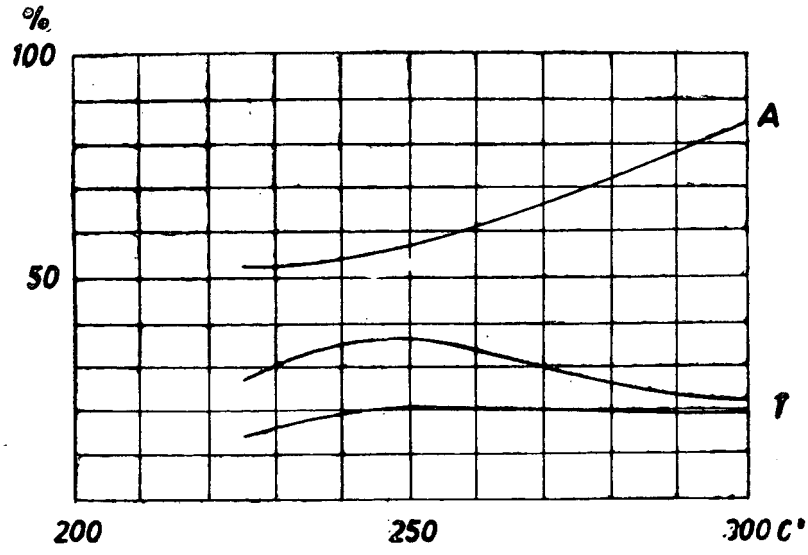

Figure 36

Dependence of the evaluation factors of furfural-furan conversion on temperature /Pb catalyst on Al_2O_3/

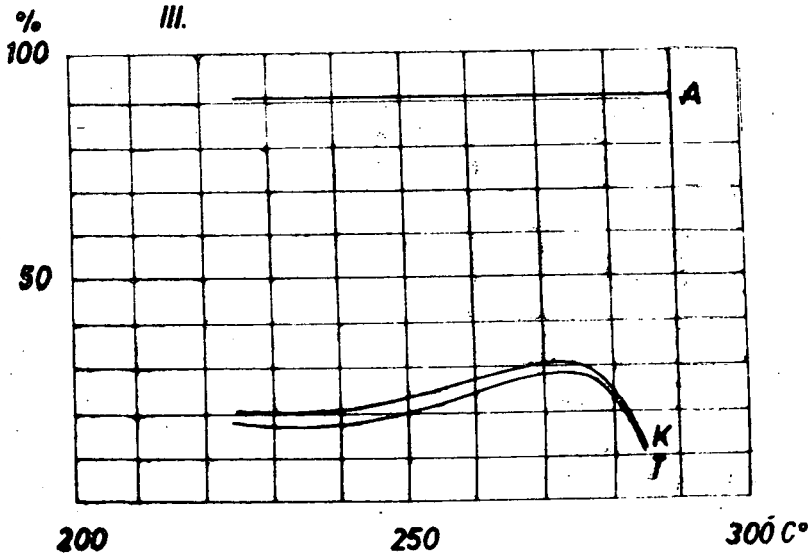

Figure 37

Dependence of the evaluation factors of furfural-furan conversion on temperature /PbO catalyst on Al-grit/

C/ EXPERIMENT FOR THE PRODUCTION OF FURAN FROM FURFURAL BY VAPOUR-PHASE HETEROGENEOUS CATALYSIS

1. Experimental conditions

The experimental conditions for the conversion of furfural into furan have been selected under consideration of the following principal parameters:

a/ Temperature
b/ Pressure
c/ Ratio and feed rates of reactants
d/ Variation of the chemical composition and method of preparation of the catalysis
e/ Selection of the material of construction of the reactor wall
f/ Determination of the maximum dimensions of the reactor

a/ The effect of temperature on the formation of furan

An examination of the correlations between conversion, material balance and temperature reveals that the process may be described by a curve of maximum type. The temperature in which the reaction takes place falls within the range from 250 to 450°C, depending on the catalyst used and on the selection of the parameters.

When using a catalyst of long service life, several consecutive experiments can be carried out for the determination of optimum temperature, without observing any interfering effect, due to the exhaustion of the catalyst, on the temperature - furan yield relation. However, exhaustion of short-life catalysts may interfere and therefore it is advisable to change the catalyst every time after establishing the volume of furan belonging to a particular temperature. In such

cases fresh portions of catalyst should be taken for every test of the series from a stock prepared in advance. The curve for the determination of optimum temperature may be plotted first on the basis of a few measured points, the number of which is then subsequently increased in the vicinity of the maximum.

b/ The effect of pressure

Furfural is converted into furan at atmospheric pressure. Reduced pressure or vacuum may bring new results, this, however, should be considered for industrial application only when outstanding advantages may be expected. The most convenient operation pressure is atmospheric pressure of about 760 Torr.

In the course of our work, first we always applied the least expensive experimental conditions to realize the processes and expensive ones promising success were tested only in cases when the first attempt failed.

c/ Ratios and feed rates of the reacting substances:

In the determination of the ratio of the components and the feed rate, it has to be established whether water is needed for the oxidation of furfural or not. Another point to be cleared up is whether oxidation can be carried out with CO_2 under formation of CO or the process may simply be carried out by using atmospheric oxygen, the required oxygen ratio being adjusted by the admixture of N_2.

As regards the ratio of furfural to water, it should be pointed out that through distillation at atmospheric pressure and addition of water the following three basic materials are readily produced:

α / Dry furfural after removal of the fore-run,
β / Furfural saturated with water,
γ / Water saturated with furfural.

From water saturated with furfural, water containing 0-8 per cent of furfural may be prepared by the addition of further quantities of water.

To determine the optimum water concentration it is advisable to prepare three or four different mixtures of water and furfural and to test them for furan production while keeping all other parameters, as far as possible, constant. Theoretically one atom of oxygen is needed for the conversion of one mole of furfural to furan carboxylic acid; in practice, however, the oxygen requirement varies with the type of catalyst and should be tested in the range between 0.25 and 3 atoms of oxygen. The deviation of the optimum oxygen ratio from the stochiometric oxygen ratio depends also on temperature.

For the feeding of liquids in the range of 0.5 to 30 ml of furfural per hour, a feeding burette equipped with a needle valve regulated with a micrometer screw is used, and for feeds within the range from 30 to 1000 ml per hour a piston feed device. The feed pump has three stages, each stage permitting regulation with a turnknob within its own limits.

In the course of the experiment the exhaustion curve of the catalyst should be observed. This curve may be plotted for each catalyst as a time-yield function. After the exhaustion of the catalyst first a small volume of air is blown through the reactor countercurrently to the direction of flow in operation. This is necessary to prevent the passing of tar products from the evaporator through the catalyst and the ignition of soot deposited on the catalyst, because these may result in a complete inactivation of the catalyst. The volume of air blown through the reactor in such cases will be expedient 20 lit/hr.

d/ Variation of the chemical composition and the method of preparation of the catalyst

As a rule, any catalyst suitable for oxidation purposes may be used for oxidative decarboxylation. By the variation of the quality, the quantity and the method of preparation countless series of various catalysts can be prepared. It is advisable to prepare in addition to a number of known catalyst types, a few catalysts on the basis of the collection of formulations and to test them for suitability in furan production /see Part III Paragraph E/6/.

e/ Selection of reactor wall material

After having established the optimum conditions for a series of experiments in a reactor of a particular wall material, it is recommended to construct identical reactors of several other materials of construction suitable to this end /iron, nickel, acid resistant steels, aluminium, eventually ceramics, etc./. The optimum of the reaction should be examined under identical conditions, possibly as a function of time. The materials of construction of the reactor yielding the best results shall be selected for the reactor wall of the planned plant. The higher the catalytic action of the reactor wall in the positive or in the negative sense, or the higher its surface referred to the unit volume of the catalyst, the less accurate experimental results will be obtained. This statement is clearly illustrated by the following example: If the reactor is made of a new iron tube with smoothly polished inner surface, the "specific surface area" of the wall will be small. Several months or even years of operation will cause the iron to corrode and approach a pyrophorous condition. This increases the surface area of the reactor wall and its chemical properties, and consequently its catalytic action.

f/ Determination of the maximum reactor dimensions

Diameter and length of the reactor will be increased gradually to determine that maximum dimension at which the organic reaction still proceeds favourably. The form thus determined is suitable for scaling up for industrial plant operation by connecting in parallel the units of the determined dimensions. This step, however, can be carried out only when optimum conditions in respect to Paragraph a/ to e/ have been already determined. Volumes II and III deal with this theme in detail.

2. Recording of experimental results

Our equipment may be considered as a complex instrument of the chemical reaction to be examined. Our reaction is subjected to examinations under various chemical and physical conditions, applying different catalysts, ratios of mixtures, pressures, temperatures, etc. Obtained numerical data on experimental behaviour are plotted in a series of two and three dimensional curves, which lend themselves to evaluation. On completing a well-planned series of experiments it can be decided whether a reaction may be carried out on an industrial scale, and, if so, the conditions of its successful operation may be predicted. For this purpose, experimental facts must first be entered on record. Recording must be accurate and scrupulous.

The absolute or relative time, all values of temperature, numerical values of pressure, burette readings, valve positions, gasometer readings, will be taken down on record. Figure 34 serves as an example for the registration of data necessary for preparing the record of experiments. Observations during the experiments should be made by an independent person. It would have been conceivable to arrange the instruments in a way which permits the photographic registration of the above data with a few photographs. This, however, would not have served our purpose.

The data in the extreme right column of the experimental record are the specific evaluation factors of our chemical reaction. This collection of data can be compiled exclusively by calculation from previous data with the help of the equations given in Paragraph 3, under utilization of the "Tables for Calculation" /Paragraph 4/. /See also Part III, Paragraphs B/8 and B/9./.

3. Calculation of the specific evaluation factors characterising the course of the reaction

In order to evaluate the course of the reaction as far as possible, independently of the apparatus, specific, dimensionless values of the conditions and of the results of the reaction must be calculated from the experimental data. Such values of specific space velocities, contact times, etc. must be used, that, after scaling up to industrial dimensions, values of conversion, production, material balance etc. will not change essentially. In literature, the names of specific values often refer to different formulae. For purposes of our special investigations, new formulae may be established and new concepts may be introduced. It is important, however, that formulae, units or concepts, linked with the single names, shall not change within the same series of experiments.

Some of the characteristics in general use will be given below by way of example. In principle, the formula of space velocity may equally be used whether furfural is measured cold in litres, or millilitres, or computed for the applied temperature in hot overheated vapour litres; catalyst volume may be expressed in litres or millilitres. Expediently, values will be given in units that may be observed directly instead of units to be computed.

Research chemists prefer to express conversion values in units of mole/mole, these being the most instructive for

them. For economic reasons, however, kg/ kg unit ratios are preferred in industry. In the first case, the maximum value of mole/mole is 1, whereas in the case of kg/kg, for instance in case of maleic anhydride formation from furfural, ratios higher than 1 are possible.

Two types of conversion are known: overall conversion /A/, and production /T/, also called useful conversion or yield

$$A = \frac{\text{furfural converted}}{\text{furfural introduced}} = \text{mole/mole /dimensionless/}$$

$$T = \frac{\text{furan formed}}{\text{furfural introduced}} = \text{mole/mole /dimensionless/}$$

In the first case the rate of conversion is characterized without taking into account the direction of the conversion, while in the second case, the grade of conversion is restricted to the reaction proceeding in the direction of useful product /furan/. The quotient of the two parameters gives the ratio of the total number of converted moles and the number of moles converted to the useful product. This is called /K/, or selectivity, chemical efficiency and by some ultimate yield.

$$K = \frac{T}{A} = \frac{\text{Furan formed}}{\text{Furfural converted}} = \text{mole/mole /dimensionless/}$$

A, T and K, multiplied by 100 give the parameters in terms of percentages. Important characteristics are also space velocity /Té/ and contact time /I/:

$$Té = \frac{\text{Furfural feed rate per hour /litre/}}{\text{Catalyst volume /litre/}}$$

$$I = \frac{\text{Catalyst volume /litre/}}{\text{Furfural feed rate per hour /litre/}}$$

In the industry the denotion specific production or output /F/ is frequently used. This denotes the rate at which a particular reactor can yield a specified product.

$$F = \frac{\text{Furan formed per hour, kg}}{\text{Overall reactor volume /litre/}} ;$$

Finally, material balance is an important characteristic permitting to control our work and to detect possible material losses /leakage/.

The definitions given above are specific, i.e. they are more or less dependent on the reactor. The definition of feed rate is:

$$\text{Feed rate} = \frac{\text{Material introduced /mole, litre, kg/}}{\text{Time /minute, second, hour/}}$$

4. Tables for Computations

In order to facilitate quick work, gram and mole values corresponding to the single ml values of initial and converted furfural, further those corresponding to the measured values of furan within the range from 0 to 100 ml are given in tabular form. Decimal fractions can be obtained by interpolation.

Table I

Furfural

ml	g	mole	ml	g	mole
1	1,1598	0,0121	7	8,1186	0,0847
2	2,3196	0,0242	8	9,2784	0,0968
3	3,4794	0,0363	9	10,4382	0,1089
4	4,6392	0,0484	10	11,6980	0,1210
5	5,7990	0,0605	11	12,7578	0,1331
6	6,9588	0,0726	12	13,9176	0,1452

ml	g	mole	ml	g	mole
13	15,0774	0,1573	48	55,6704	0,5808
14	16,2372	0,1694	49	56,8302	0,5929
15	17,3970	0,1815	50	57,990	0,6050
16	18,5568	0,1936	51	59,1498	0,6171
17	19,7166	0,2057	52	60,3096	0,6292
18	20,8767	0,2178	53	61,4694	0,6413
19	22,0362	0,2299	54	62,6292	0,6543
20	23,1960	0,2420	55	63,7890	0,6655
21	24,3558	0,2541	56	64,9488	0,6776
22	25,5156	0,2662	57	66,1086	0,6897
23	26,6754	0,2783	58	67,2684	0,7018
24	27,8352	0,2904	59	68,4282	0,7139
25	28,9950	0,3025	60	69,5880	0,7260
26	30,1548	0,3146	61	70,7478	0,7381
27	31,3146	0,3267	62	71,9076	0,7502
28	32,4744	0,3388	63	73,0674	0,7623
29	33,6342	0,3509	64	74,2272	0,7744
30	34,7940	0,3630	65	75,3870	0,7865
31	35,9358	0,3751	66	76,5468	0,7986
32	37,1136	0,3872	67	77,7066	0,8107
33	38,2734	0,3993	68	78,8664	0,8228
34	39,4332	0,4114	69	80,0262	0,8349
35	40,5930	0,4235	70	81,1860	0,8470
36	41,7528	0,4356	71	82,3458	0,8591
37	42,9126	0,4477	72	83,5056	0,8712
38	44,0724	0,4598	73	84,6654	0,8833
39	45,2322	0,4719	74	85,8252	0,8954
40	46,3920	0,4840	75	86,9850	0,9075
41	47,5518	0,4961	76	88,1448	0,9196
42	48,7116	0,5082	77	89,3046	0,8317
43	49,8714	0,5203	78	90,4644	0,9438
44	51,0312	0,5324	79	91,6242	0,9559
45	52,1910	0,5445	80	92,7840	0,9680
46	53,3508	0,5566	81	93,9438	0,9801
47	54,5106	0,5687	82	95,1036	0,9922

ml	g	mole	ml	g	mole
83	96,2634	1,0043	92	106,7016	1,1132
84	97,4232	1,0164	93	107,8614	1,1253
85	98,5830	1,0285	94	109,0212	1,1374
86	99,7428	1,0406	95	110,1810	1,1495
87	100,9026	1,0527	96	111,3408	1,1616
88	102,0624	1,0648	97	112,5006	1,1737
89	103,2222	1,0769	98	113,6604	1,1858
90	104,3820	1,0890	99	114,8202	1,1979
91	105,5418	1,1011	100	115,9800	1,210

Table II

Furan

ml	g	mole	ml	g	mole
1	0,9365	0,01377	21	19,6665	0,28917
2	1,8730	0,02754	22	20,6030	0,30294
3	2,8095	0,04131	23	21,5395	0,31671
4	3,7460	0,05508	24	22,4770	0,33048
5	4,6825	0,06885	25	23,4125	0,34425
6	5,6190	0,08262	26	24,3490	0,35802
7	6,5555	0,09639	27	25,2855	0,37179
8	7,4920	0,11016	28	26,2220	0,38556
9	8,4285	0,12393	29	27,1585	0,39933
10	9,3650	0,13770	30	28,0950	0,41310
11	10,3015	0,15147	31	29,0315	0,42687
12	11,2380	0,16524	32	29,9680	0,44064
13	12,1745	0,17901	33	30,9045	0,45441
14	13,1100	0,19278	34	31,8470	0,46818
15	14,0475	0,20655	35	32,7775	0,48195
16	14,9840	0,22032	36	33,7140	0,49572
17	15,9205	0,23410	37	34,6505	0,50949
18	16,8570	0,24786	38	35,5870	0,52326
19	17,9350	0,26163	39	36,5235	0,53703
20	18,7300	0,27540	40	37,4600	0,55080

ml	g	mole	ml	g	mole
41	38,3965	0,56457	71	66,4915	0,97767
42	39,3330	0,57834	72	67,4280	0,99144
43	40,2695	0,59211	73	68,3645	1,00521
44	41,2060	0,60588	74	69,3010	1,01898
45	42,1425	0,61965	75	70,2375	1,03275
46	43,0790	0,63342	76	71,1740	1,04652
47	44,0155	0,64791	77	72,1105	1,06029
48	44,9520	0,66096	78	73,0470	1,07406
49	45,8885	0,67473	79	73,9835	1,08783
50	46,8250	0,68850	80	74,9200	1,10160
51	47,7615	0,70227	81	75,8565	1,11537
52	48,6980	0,71604	82	76,7930	1,12914
53	49,6345	0,72981	83	77,7295	1,14291
54	50,5710	0,74358	84	78,6660	1,15668
55	51,5075	0,75735	85	79,6025	1,17045
56	52,4440	0,77112	86	80,5390	1,18422
57	53,5805	0,78489	87	81,4755	1,19799
58	54,3170	0,79866	88	82,4120	1,21176
59	55,2535	0,81243	89	83,3485	1,22533
60	56,1900	0,82620	90	84,2850	1,23930
61	57,1265	0,83997	91	85,2215	1,25307
62	58,0630	0,85374	92	86,1580	1,26684
63	58,9995	0,86751	93	87,0945	1,28601
64	59,9360	0,88128	94	88,0310	1,29438
65	60,8725	0,89505	95	88,9675	1,30815
66	61,8090	0,90882	96	89,9040	1,32192
67	62,7455	0,92259	97	90,8405	1,33569
68	63,6820	0,93636	98	91,7770	1,34946
69	64,6185	0,95013	99	92,7135	1,36323
70	65,5550	0,96390	100	93,6500	1,37700

5. Catalysts[x]

The function of the catalyst is manifested partly in the fixing, the adsorbing of the reactant on its surface. Owing to this, a thin film is formed on the surface of the catalyst in which the concentration of the reactant is much higher than in the reaction space. Therefore, the surface area of the catalyst is of primary importance as regards the rate of the reaction.

However, the surface area of the catalyst is not the only decisive factor to determine the characteristics of the catalyst. Adsorption power, the crystal and electron structures of the catalyst and some other factors must also be taken into consideration.

The action of the catalyst may consist besides the producing a high concentration of reactants on its surface, also in the changing the electron configuration of the reactant /or the reactants/ adsorbed by chemisorption and to improve hereby the energetical conditions from the point of view of the proceeding of the reaction.

The intensity of sorption may determine the efficiency of the catalyst. If binding is weak, the concentration of the intermediate complex formed by sorption is low and the effect of the catalyst on the molecules of the sorbate may be slight, while a too intensive binding may cause irreversible sorption, which means that the molecules remain fixed on the surface. Both extreme cases result in a reduction or even in the disappearance of the catalytic action.

The rate of reaction cannot be characterized by the quantity of catalyst, since in heterogeneous catalysis the catalyst does not participate in the reaction with its whole mass. The

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[x] For theory pertinent to catalysis see Part II, A. and B.

larger and the more easily accessible is the surface of the contact material, the higher is its catalytic activity. The principal characteristics of catalytic activity are:

a/ specific surface
b/ spatial discontinuities on the surface of the contact material
c/ the strength of binding established between substrate and catalyst
d/ the electron structure of the contact material.

The surface of the catalyst may be:

Surface of 1st order: coarse surface, internal cavities, interstices, channels of macroscopic and microscopic dimensions /≧ 500 mμ/, further the whole external surface;

Surface of the 2nd order: the surface of submicroscopical /10 mμ - 500 mμ/ interstices, channels, capillaries;

Surface of 3rd order: the surface of amicroscopical /≦ 1 mμ/ channels and interstices/.

Surfaces of 1st and 2nd order are easily accessible for gas molecules, and reaction products can leave them unhindered. Surfaces of 3rd order are reached only slowly by molecules, and amicroscopical interstices may get clogged. These surfaces are therefore less active than those of 1st and 2nd order.

6. Requirements in respect to catalysts

As regards appearance, catalysts may be formed /for instance, pellets/, lumpy, granulated or in case of metals, nets woven of fine wire, etc.

With consideration to their chemical composition metals and metal oxides are most frequently used as contact catalysts. A catalyst selected for industrial use should meet the following requirements:

a/ The catalyst should be prepared possibly of an inexpensive and easily available substance.

b/ The catalyst should not be sensitive to catalyst poisons.

c/ The catalyst should be resistant to heat, temperature changes and slight overheating without losing its advantageous physical and chemical characteristics.

d/ The catalyst should possess certain mechanical strength and durability.

e/ The catalyst should increase only the rate of the principal reaction i.e. it should be selective.

f/ The preparation of the catalyst should be reproducible and its activity constant during use.

g/ The catalyst should not age rapidly, it should have a long service life, and should not be liable to recrystallization. No carbon deposits shall form on its surface during use. Its activity should not decrease with time, it should be readily and quickly regenerable: time required for regeneration should be a low percentage of the operating cycle. The catalyst should not attack the reactor walls.

h/ The catalyst should not be sensitive to overloading.

i/ The catalyst should not be harmful to the health of the handling personel. When the use of chemically advantageous materials becomes unavoidable, the production must afford economically the costs of efficient health protection equipment.

Any undesirable property of the catalyst may be accepted if the economy of the production permits it.

The requirements to be met by the catalysts might seem contradictory: the best compromise will be selected under consideration of the economical aspects of production.

The complete vapour-phase heterogeneous catalytic laboratory lends itself to the evaluation of catalyst properties. Some of the undesirable properties, even if they cannot be eliminated, may be evaded by adequate measures. In the theoretical part /see Part I, C/ mention has been made of furan production over pyrophorous lead catalyst. In this case the poor mechanical strength of the catalyst could be compensated by the use of small ceramic trays.

7. Preparation of catalysts

The substances, mostly salts, used in the preparation of catalysts, are dissolved in water and precipitated with alkali hydroxide, carbonate or hydrocarbonate in form of hydroxy carbonates or basic carbonates. Another method for the preparation of catalysts is the thermal decomposition of the initial metal salt to obtain a finely dispersed metal oxide. The desired catalytic metal surface can be obtained also by the reduction of metal oxides.

The same methods are used in the production of mixed catalysts. The quality of a catalyst, i.e. the activation of the contact material, depends on the conditions of precipitation. Chief possible influencing variables are:

a/ temperature,
b/ concentration,
c/ rate of precipitation,
d/ mode of precipitation.

In general, dispersivity of the precipitate will be high, i.e. favourable for catalysis, if the temperature of precipitation is low, the process is quick, and the solution is not too diluted.

Mixed catalysts can be prepared by one of the following methods:

a/ Co-precipitation

b/ Precipitates prepared separately are suspended in aqueous medium, then mixed.

c/ Dry lumpy catalyst is impregnated with another substance.

The catalytic effect of mixed catalysts shows wide variations. In addition to the catalytic effect of the single components of the mixture, important changes in the specific surface area of the formed mixture may occur, and the contact of the components may result in new properties.

When selecting the types of catalyst to be used in furan production, our aim was to find catalysts which, besides being easy to handle and suitable on laboratory scale, meet also industrial requirements.

As regards catalyst efficiency, the conditions of preparation are of first-rate importance, and the reproduction of these conditions generally presents difficult problems to the chemist. Chemical composition, quality and quantity of contaminations in the initial materials, sequence, time, and temperature of the carrying out of the chemical and physical formulation steps, geometric, pressure and other conditions of pelletizing or of forcing through a slit, temperature and time parameters of drying and heating, conditions of heat treatment in hydrogen, oxygen or steam, chemical modifications produced in these operations, reaction heat generated in the production of the catalyst, and a host of other, known and even unknown factors offer an almost infinite number of combination, of which that ensuring optimum specific surface, crystal structure, etc. for the acceleration of the reaction in question must be selected. Reproducible geometrical and

heat conductivity data of the catalyst facilitate the computations required in the designing of the dimensions of the industrial plant.

The following examples serve to illustrate the above-said. Let us assume that solutions "A" and "B" have to be mixed to obtain a precipitate "C", the catalyst. The conditions of production of "C" will vary depending on "A" being poured into "B" or conversely, as relative concentrations and their continuous variation in time will be different in the two cases. Owing to this, the microscopic crystal structures of the precipitates will not be uniform. If components "A" and "B" are dosed simultaneously at a constant rate, under vigorous stirring, into a small mixing space, maintaining a continuous flow, the conditions of production will improve suddenly.

In another case the pulverized materials "D", "E" and "F" are to be mixed in order to produce catalyst "G", and the reaction proceeds say at 300°C in 25 days. If the temperature is raised by +50°C, the reaction starts spontaneously and the mixture warms up in a short time, to 600 - 700°C. Thougha chemical composition identical to that of "G" is obtained in this way, the crystal structure of the catalyst will be unsatisfactory, as - owing to the high temperature - crystal edges and peaks melt, and the active sites are practically reduced to zero. A reaction proceeding slowly at low temperature results, in turn, in an optimum crystal structure. Evidently such catalyst is expensive and should be used only if the object cannot be attained with a cheaper catalyst, more economical to produce.

8. Catalysts in operation

The grain size of the catalyst is selected to suit the cross section of the reactor. The lowest catalyst content is to be found in the catalyst space close to the reactor wall, as

extreme catalyst particles are surrounded on the side of the wall by relatively large channels, whereas towards the centre, interstices between the grains are partly filled up by the projecting corners of other grains.The percentual volume of the cylindrical ring of catalyst, 1/2 d /where d is the average diameter of the grain of the catalyst, referred to the volume v of the catalyst-space/, will be the higher, the higher the value of d and the lower that of v. Therefore, it is desirable to reduce the diameter of the catalyst within reasonable limits.

One tenth to one twentieth part of the reactor diameter is considered as the optimum grain diameter. The increasing resistance to flow of the medium limits the reduction of d to a value below which pulverulence will clog the reactor. A good catalyst has a visible coarse surface and very large specific surface area. It is very favourable, when the contact between gases and catalyst is facilitated by channels, similar in principle to the structure of animal lungs.

Catalyst substance recrystallizes during operation.Its peaks and edges become blunt. The number of active points responsible for catalysis decreases, the microstructure of the catalyst changes and the production rate per hour drops. This state is called the ageing of the catalyst.A decrease in the efficiency of the catalyst may also be due to irreversible poisoning. Visible accumulation of tar or carbon on the catalyst surface may also cause the failure of catalyst. In this case organic matters must be removed from the catalyst surface. This is usually done by cautious burning, because a drastic burning would melt the edges of the microcrystals and destroy the catalyst. The catalysts may be regenerated also by chemical and physical processes, such as heating in a current of hydrogen, air, etc. After this activation catalysts become suitable again for the catalysis of organic reactions.In many instances, operating and regeneration tem-

peratures are different.This is a great disadvantage already in laboratory work, and even more so in industrial operation, because, due to its dimensions, a plant reactor has a higher thermal inertia.

In catalyst research, the catalysts found most suitable must be tested for service life. This involves the production and regeneration of a small amount of catalyst for several weeks or months until production becomes economic. Naturally the catalyst of the most favourable service life will be used in the experiments for the scaling-up of the catalyst zone to industrial dimensions.

Many hundred and sometimes even many thousand catalysts have to be tested until an industrially suitable catalyst is found for a particular reaction. A catalyst that has stood the test as regards chemical composition and mechanical strength must be subjected to exhaustion tests. In a small reactor, the catalyst is put to work for long production periods and the production/time curves are analysed.Obviously, the catalyst must be regenerated during this period.Vanadium pentoxide catalyst, for instance, is sometimes excessively active in the beginning for a few months and overoxidizes therefore one part of the material, thus working with a poor yield; later, optimum operation is attained.Sometimes it may be used satisfactorily for several years and deteriorates only afterwards. Metal chromite catalysts,on the other hand, behave unfavourably, particularly in the very case of furan.

Operations between two regeneration periods will be investigated on Fig. 38 from the point of view of change in temperature, work requirement and regeneration. The reactor must be cooled down from 400°C in eight hours then it must be heated with air in order to burn off carbon deposited on the catalyst surface. After a few hours of cautious burning, carbon is removed and moreover, the catalyst attains a higher

oxidation state. Next, the catalyst is cooled down in eight hours and when cold, a hydrogen stream is started to warm up the apparatus and, after the reduction of the catalyst, it is cooled again in a hydrogen stream. After cooling, hydrogen stream is cut off, and, after heating up, the useful reaction time follows, then the cycle begins again. It may be seen

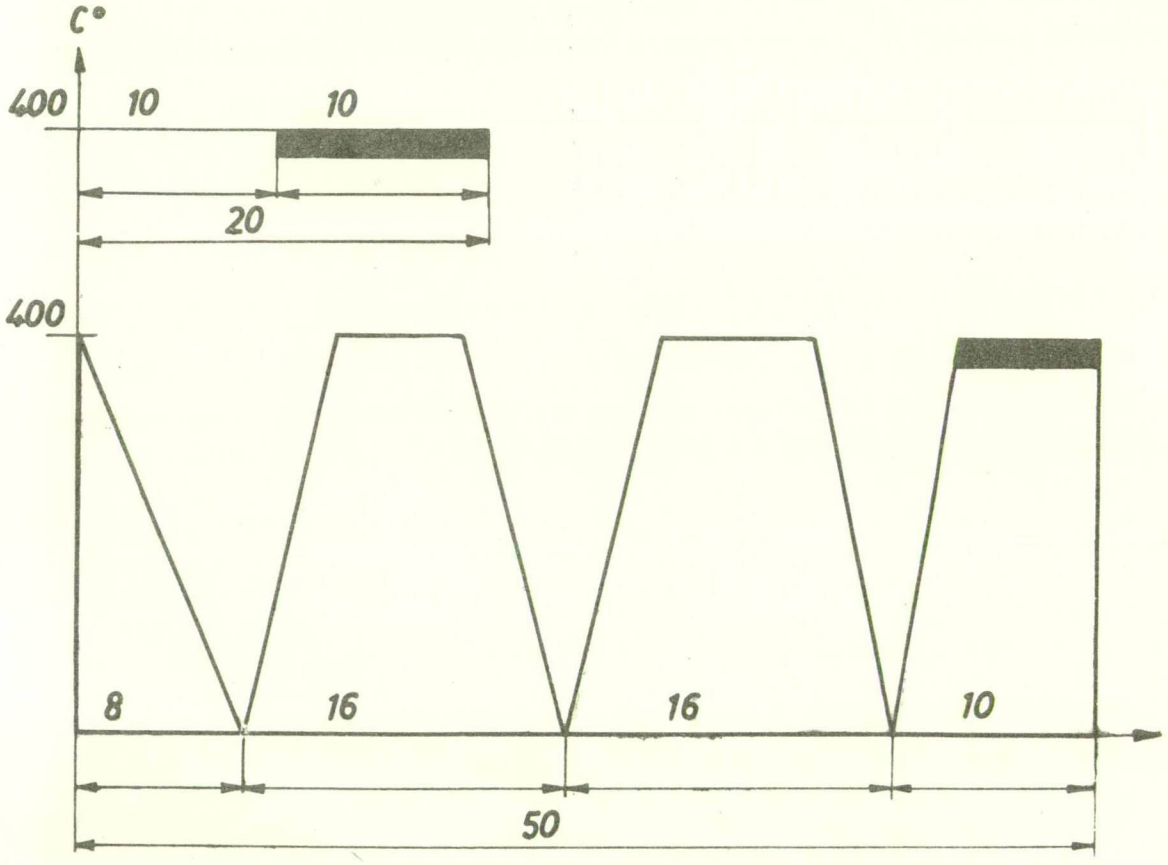


Figure 38
Working and regenerating periods of lead oxide catalyst

that the production time is only 20 per cent of the whole period. When the period is repeated for a week, the catalyst

becomes completely exhausted. This catalyst is therefore unsuitable for plant experiments.

In the upper example of Fig. 38 regeneration and reaction periods for a lead oxide type total 20 hours, and production time amounts to 50 per cent of the cycle. One of the aspects for the evaluation of a catalyst is the above ratio cycle time:reaction time, further the empirical examination of the time of exhaustion of the catalyst.

The capacity of a catalyst, i.e. the quantity of product obtained with one litre of catalyst per hour, depends on the combined effect of the grain size, uniformity, density, compaction, specific surface area, concentration and activity of the catalyst. Naturally, the higher the capacity of a catalyst, the higher the heat source density in the reaction zone, resulting in a rise in temperature in exothermal reactions and in a decrease in temperature in endothermal reactions. A catalyst will have maximum capacity when used in a self-carrier form; obviously, in this case, heat dissipation will be the hardest problem to solve.

With exothermal reactions, catalyst concentration and production rate may be selected so that the heat of reaction evolved in unit time will be equal to the loss of the heat of the system referred to the same unit of time. In this case the reactor once started does not require any further heat supply and this kind of operation is, therefore, economical.

Reaction gas mixtures may be diluted with inert gases to reduce the spatial heat source density both in the production period and in the mild burning off period of carbon. CO_2, N_2, and steam are most frequently used to this end. A great advantage of steam is that in case of substances of high vapour tensions, such as for example furan, separation may be attained by simple cooling. When regenerating vanadium pent-

oxide, air must be diluted, since otherwise overactivation occurs which, due to overburning, reduces the yield.

9. Selection of the material of construction of the reactor wall

As material of construction for reactor wall, primarily Ni, acid resistant steel, Al, and Fe come into consideration. Our reactor was made of Ni and acid resistant steel, respectively, because the disadvantageous effect of the walls /see Part III, Paragraph C/1.e/ is the least pronounced in the case of these metals. If the wall of the reactor is made of plain iron, later it becomes first rusty, then pyrophorous. Thus, catalytic properties of the wall change in this case in time.

D/ PRODUCTION OF FURAN WITH METAL OXIDE CATALYSTS

1. The preparation of metal oxides from metals with gaseous oxygen

The formation of metal oxides /among which the oxides of Pb, Bi, Zn, Sn, Cd, Hg, and Ag are the most important from the point of view of our present investigations/ from their elements is an exothermic process, that is to say, these metals are oxidized by air /see Table 3/. When air is bubbled through the molten metal, the oxide of the metal forms. The rate of oxidation does not depend primarily on thermodynamic factors /because the formation of the oxides in question - with the exception of Hg and Ag - is accompanied by the evolution of appreciable quantities of heat in the exothermic reaction/, but is determined rather by kinetic parameters. The rate of oxidation increases rapidly with increasing temperature. In the order of increasing heats of formation, the oxides in question may be arranged in the following series:

$$ZnO > SnO > CdO > PbO > Bi_2O_3 > HgO > Ag_2O.$$

In establishing this order, 1/3 of the heat of formation of Bi_2O_3 was taken into consideration to permit a direct comparison with the other oxides. The melting point of silver is substantially higher than that of the other listed metals and its oxide decomposes at a temperature much lower than the melting point /200°C/. In view of this fact and of the but weakly exothermic character of the heat of formation of the oxide, no further study will be made of the oxidizability of silver.

As first approximation, the above order corresponds to the order of thermal stability of the metals in question. As

mentioned already, Ag_2O decomposes at about 200°C, HgO decomposes readily at 400°C, etc. On advancing in the series, oxides become gradually more stable.

When air is bubbled through a multicomponent metal melt, first the metal showing the greatest affinity towards oxygen will be oxidized. Affinity to oxygen is determined by two factors: the normal affinity of the metal and its concentration. Concentrations being equal, first the metal of higher normal affinity, to which the lowest partial pressure of oxygen appertains, will be oxidized. The oxygen pressure at equilibrium with the metal and its oxide at a given temperature is a measure of the affinity to oxygen.

Example: Let us assume that a metal melt contains three components /A, B, and C/ in a percentage ratio m, n, and o /Fig. 39/. The order of normal affinities can be established on the basis of the desorption curves /in Fig. 39 curves /A/, /B/, and /C/, as A > B > C. Though metal A has the highest normal affinity, first metal B will be oxidized, because, due to its higher concentration, a lower oxygen pressure $/O_2/_B$ will result in the metal melt /see Fig. 39/, that is to say, it has a higher affinity to oxygen. Pure B-oxide will separate until the concentration of metal B is reduced to a value at which $/O_2/_B$ becomes equal to the equilibrium oxygen pressure of the next metal-metal oxide system, in the present case to $/O_2/_A$. From this time on, metals A and B will be oxidized simultaneously, until, owing to a decrease in their concentration, their corresponding oxygen pressure will attain a value equal to $/O_2/_C$. From this point on, all three metal oxides are formed together.

The situation becomes more simple if the metal melt contains the components in an equal proportion. The order of sequence of oxidation is determined by the order of normal affinities. By way of example, let us start from a melt containing Bi,

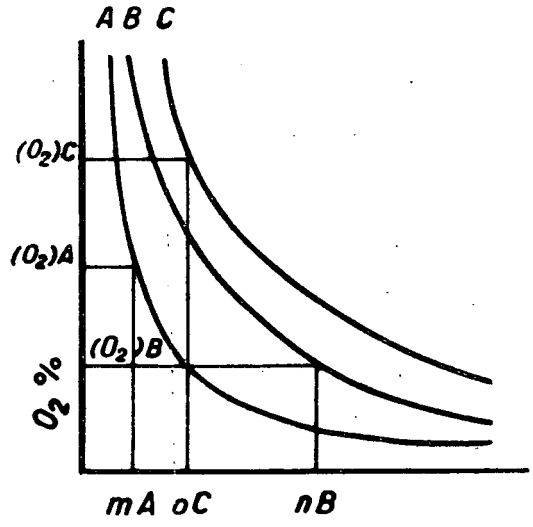


Figure 39

The formation of oxides in metal mixtures /curves of normal affinity/

Zn, Sn, Cd, and Pb, in equal proportions, and let us assume that the order of normal affinities is the same as that of the heats of formation. On bubbling air through the melt, first ZnO will separate /having the highest heat of formation/, then, from a point on, determined by normal affinities, also Sn will begin to separate, next, the formation of CdO begins, that is to say, at this stage ZnO + SnO + CdO separate already together, etc. Thus, oxidation proceeds on the basis of the heats of formation in the following order:

$$Zn > Sn > Cd > Pb > Bi > Hg.$$

A similar order /with a single exception/ is obtained if these metals are arranged in the order of normal potential/one

electron transition:

Zn/+0,38 V/>Cd/+0,20 V/>Sn/+0,07 V/>Pb/+0,06 V/>Bi/-0,09 V/.

In the above considerations, no attention was paid to the interaction of the separated oxides with the metal melts.

Concerning the changes in systems composed of metal melts and metal oxides, essentially the order given above is valid. It may be expected on the basis of exclusively thermochemical considerations that the melt of a metal ahead in the series will be oxidized at a sufficiently high temperature in the presence of an oxide of a metal following it in the series. Thus, the reaction

$$Zn + PbO = ZnO + Pb$$

is exothermic, its normal affinity is positive, and therefore it proceeds spontaneously in the indicated direction. It should be mentioned, however, that even if the thermochemical conditions for the proceeding of a reaction exist, that is to say, the reaction may proceed spontaneously in the indicated direction, it does not follow that it will actually take place at a satisfactory rate under the given conditions. Besides thermodynamical factors also kinetic parameters must be considered.

2. Oxidizability of metals by carbon dioxide

The oxidation of the studied metals /Pb, Bi, Zn, Sn, Ag, Cd, and Hg/ with carbon dioxide proceeds considerably more difficultly, than the formation of the same oxides from their elements. As shown in Table 4, only the oxidation with carbon dioxide of zinc and tin is accompanied by the evolution of heat. It follows from this, as also otherwise evident, that, from the point of view of metal oxide formation, preference should be decidedly given to oxidation with gasous oxygen over oxidation with carbon dioxide.

Table 3

Formation of metal oxides from the elements

298°K				623°K			
		yellow				yellow	
$Pb_{/s/}$ + 1/2 $O_{2/g/}$	⟶	$PbO_{/s/}$	+ 52,1 kcal	$Pb_{/l/}$ + 1/2 $O_{2/g/}$	⟶	$PbO_{/s/}$	+ 52,7 kcal
$2Bi_{/3/}$ + 3/2 $O_{2/g/}$	⟶	$Bi_2O_{3/s/}$	+ 137,9 "	$2Bi_{/l/}$ + 3/2 $O_{2/g/}$	⟶	$Bi_2O_{3/s/}$	+142,1 "
$Zn_{/s/}$ + 1/2 $O_{2/g/}$	⟶	$ZnO_{/s/}$	+ 83,2 "	$Zn_{/g/}$ + 1/2 $O_{2/g/}$	⟶	$ZnO_{/s/}$	+ 84,2 "
White /β/				$Zn_{/l/}$ + 1/2 $O_{2/g/}$	⟶	$ZnO_{/s/}$	+ 85,9 "
$Sn_{/s/}$ + 1/2 $O_{2/g/}$	⟶	$SnO_{/s/}$	+ 68,4 "	$Sn_{/l/}$ + 1/2 $O_{2/g/}$	⟶	$SnO_{/s/}$	+ 71,6 "
$2Ag_{/s/}$ + 1/2 $O_{2/g/}$	⟶	$Ag_2O_{/s/}$	+ 7,3 "	Ag.m.p. 961°C; Ag_2O decomposes at 300°C			
$Cd_{/s/}$ + 1/2 $O_{2/g/}$	⟶	$CdO_{/s/}$	+ 65,9 "	$Cd_{/l/}$ + 1/2 $O_{2/g/}$	⟶	$CdO_{/s/}$	+ 62,0 kcal
		yellow				red	
$Hg_{/l/}$ + 1/2 $O_{2/g/}$	⟶	$HgO_{/s/}$	+ 21,6 "	$Hg_{/l/}$ + 1/2 $O_{2/g/}$	⟶	$HgO_{/s/}$	+ 21,4 "

+ Heat of formation at 693°K

Table 4

Oxidizability of metals with carbon dioxide

298°K		623°K	
$Pb/s/ + CO_2/g/ \rightarrow$ yellow $PbO/s/ + CO/g/$	- 15,6 kcal	$Pb/l/ + CO_2/g/ \rightarrow$ yellow $PbO/s/ + CO/g/$	-15,2 kcal
$2Bi/s/ + 3CO_2/g/ \rightarrow Bi_2O_3/s/ + 3CO/g/$	- 65,0 "	$2Bi/l/ + 3CO_2/g/ \rightarrow Bi_2O_3/s/ + 3CO/g/$	-61,8 kcal
$Zn/s/ + CO_2/g/ \rightarrow ZnO/s/ + CO/g/$	+ 15,5 "	$Zn/s/ + CO_2/g/ \rightarrow ZnO/s/ + CO/g/$	+15,1 "
		$Zn/l/ + CO_2/g/ \rightarrow ZnO/s/ + CO/g/$	+16,4 "
white /β/ $Sn/s/ + CO_2/g/ \rightarrow SnO/s/ + CO/g/$	+ 0,8 "	$Sn/l/ + CO_2/g/ \rightarrow SnO/s/ + CO/g/$	+ 3,7 "
white /β/ $Sn/s/ + 2CO_2/g/ \rightarrow SnO_2/s/ + 2CO/g/$	+ 3,5 "	$Sn/l/ + 2CO_2/g/ \rightarrow SnO_2 + 2CO/g/$	+ 5,2 "
$2Ag/s/ + CO_2/g/ \rightarrow Ag_2O/s/ + CO/g/$	- 60,3 "	A g.m.p.= 961°C, Ag_2O decomposes at 300°C	
$Cd/s/ + CO_2/g/ \rightarrow CdO/s/ + CO/g/$	- 6,8 "	$Cd/l/ + CO_2/g/ \rightarrow CdO/s/ + CO/g/$	- 5,9 "
$Hg/l/ + CO_2/g/ \rightarrow$ yellow $HgO/s/ + CO/g/$	- 46,1 "	$Hg/l/ + CO_2/g/ \rightarrow$ red $HgO/s/ + CO/g/$	- 46,5 "

+ Heat of reaction at 693°K

Table 5

Oxidizability of furfural with metal oxides at 298°K

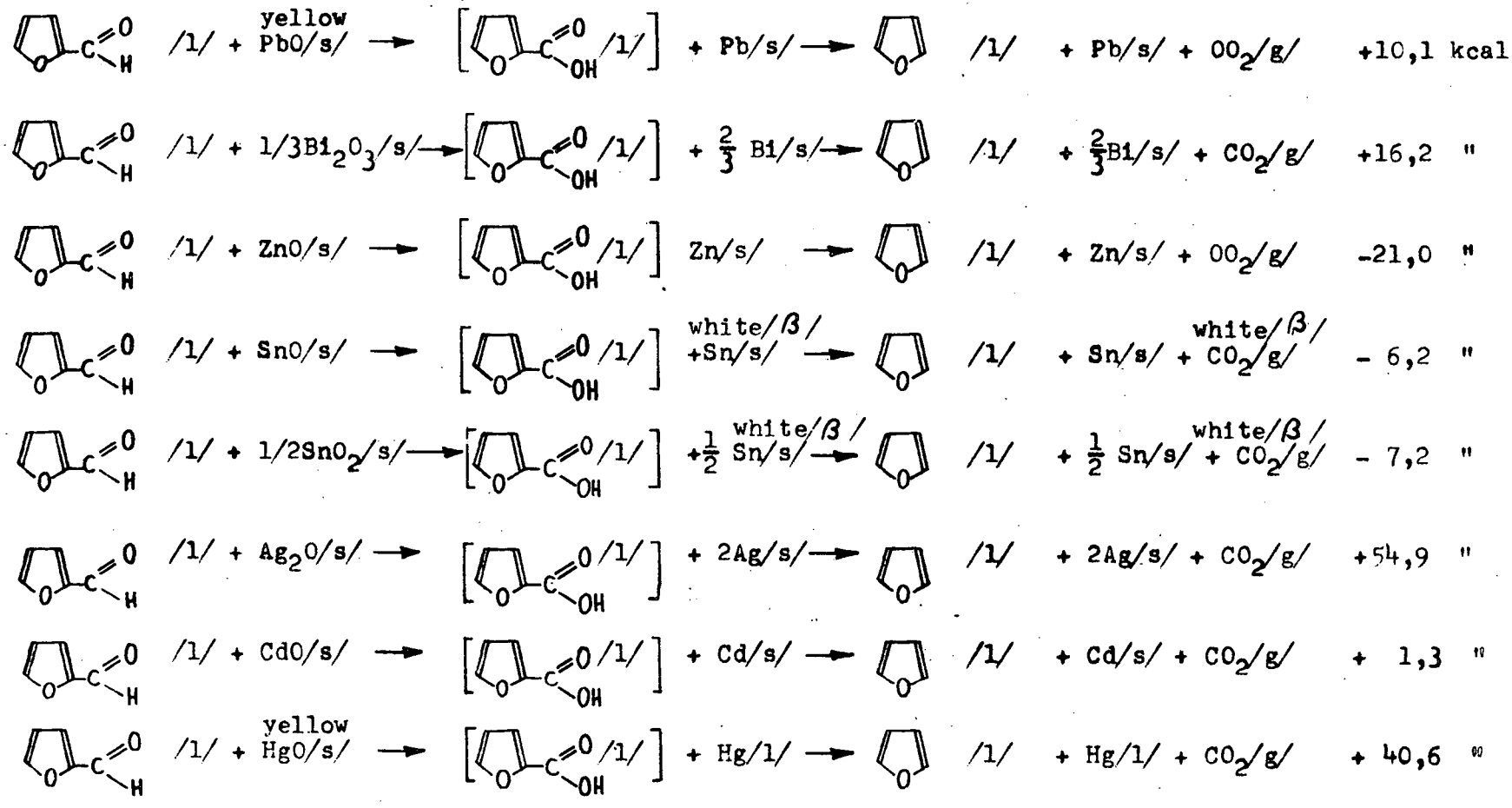
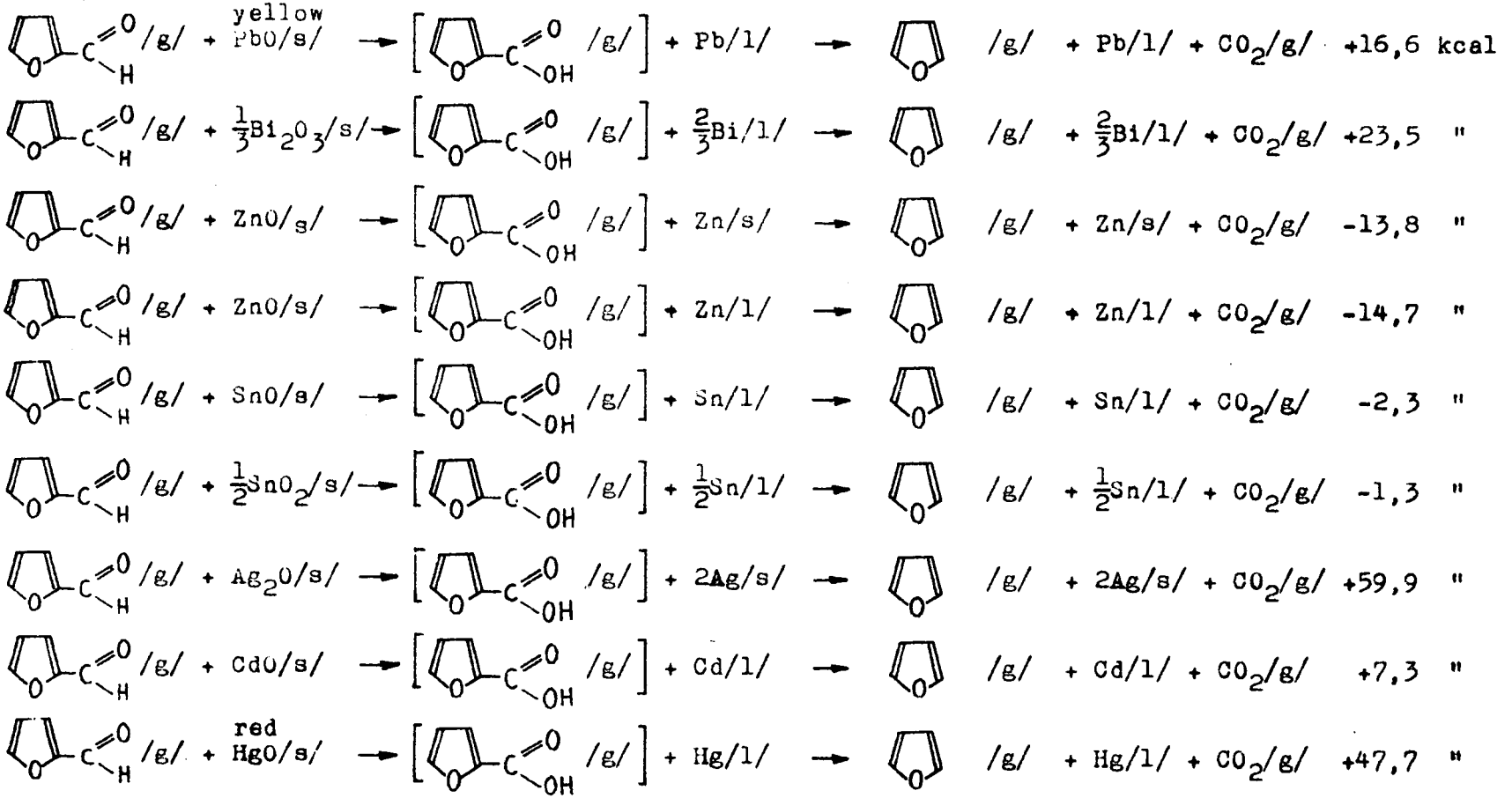


Table 6

Oxidizability of furfural with metal oxides at 623°K



3. Oxidation of furfural with metal oxides

Data in Tables 5 and 6 show that among the discussed metals /Pb, Bi, Zn, Sn, Ag, Cd, Hg/ the oxides of Ag, Bi, Pb, Cd, and Hg oxidize furfural to furan. These metals, with the exception of silver, are in a molten state at 350°C, and oxidation can be carried out in the presence of air. At this temperature, Ag is already unstable, decomposing above 200°C.

From Tables 5 and 6 it becomes evident that, with a view to the oxidation of furfural, metal oxides to be considered the most advantageous should meet the following two requirements:

a/ At a temperature above the melting point of the metal the thermal stability of the oxide permits its accumulation in appreciable quantities.

b/ The bond between oxygen and metal in the oxide shall be sufficiently weak to result in an adequately high oxidizing capacity for the organic molecule.

Among the discussed metals, silver does not meet the first requirement, while zinc and tin do not meet the second.

As mentioned already /see Part I, C/, with the redox systems Pb/PbO and Hg/HgO, we prepared furan from furfural. The use of lead catalyst led to the development of the lead melt bed reactor, and that of the mercury catalyst to the construction of the mercury vapour bed reactor.

4. The redox system Hg/HgO

Certain chemical properties of mercury can be compared with those of the noble metals. On comparing the free enthalpy of formation of different metal oxides, HgO is found to possess a high oxygen donor capacity.

Free enthalpy of formation of a few metal oxides:

Compound	kcal/mole
ZnO	76,5
PbO	52,34
HgO	13,97
Ag_2O	2,6

Hg occurs in two forms. If $HgCl_2$ or another mercuric salt is treated carefully with an excess of cold alkali, $Hg/OH/_2$ is formed, which decomposes immediately to give yellow HgO:

$$HgCl_2 + 2\ NaOH \longrightarrow HgO + H_2O + 2\ NaCl$$

Yellow HgO forms quadratic lamellar crystals. Heated to higher temperatures, it is converted to monocline red HgO. Red HgO may be obtained directly by treating mercury salts with OH ions at higher temperatures.

Red HgO is formed also at temperatures above 300°C, when oxygen reacts with metal mercury. Thus, in our case, the red modification of HgO is to be expected.

Depending on the temperature and on the pressure of oxygen, an equilibrium is established between mercury, oxygen, and the formed mercury oxide. The equilibrium

$$Hg + O \rightleftharpoons HgO$$

may be influenced, therefore, by these two factors. The dissociation of HgO has been studied in detail by Pelalon /1899/. The dissociation pressure /p/ of oxygen, formed in the presence of saturated Hg vapour from red HgO, can be described by the following expression:

$$\log p = \frac{m}{T} + n \log T + z$$

where:

$$m = -27569$$
$$n = -57,58$$
$$z = +203,947$$

In the following, the combined pressure of Hg and O_2, formed by the dissociation of red HgO at different temperatures, is given:

$$HgO_{/red/} \longrightarrow Hg_{/g/} + 1/2\ O_{2/g/}$$

T = °K	Hg + O_2 pressure, atm
633,1	0,1185
673,1	0,3040
713,1	0,8450
733,1	1,339
743,1	1,679
753,1	2,081

X-Ray diffraction investigations show the crystal structure of HgO to be a zickzack chain:

$$- Hg - O - Hg - O - Hg - O - Hg -$$

The valence angle of the bond Hg - O - Hg is 109°, while that of the O - Hg - O linkage 179°. HgO spacing in the chain is 2,03 Å, and between the chains 2,82 Å. Valence angles of the structure indicate a tetrahedric hybridization of oxygen atoms.

5. Organic catalytic oxidation reactions with mercury catalyst

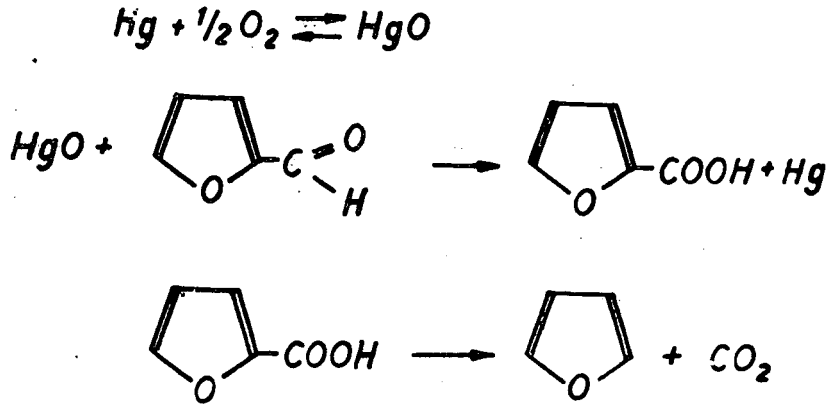
Though mercury is used extensively in the most various fields of organic chemistry, an application of the type described in the present Operator's Manual has not been yet reported in literature.

As a further development of the lead melt bed reactor, described shortly in the foregoing /see Part I, Paragraphs C/1 and 2/, experimental work on the mercury vapour bed reactor as a novel type of reactor appeared to be promising. With this reactor of principally new type, the redox potential of the system Hg/Hg^{2+} has to be taken into consideration. Oxygen transfer is dependent on the equilibrium system

$$Hg + 1/2\ O_2 \rightleftharpoons HgO,$$

and is influenced by the thermal decomposition of the formed HgO.

It follows from this that in the oxidation with mercury oxide catalyst conditions permitting with maximum possibility the formation of mercury oxide and mercury oxide concentrations of an as far as possible stationary nature are to be maintained. Our experiments showed that furan can be produced in a good yield from furfural at a temperature range between 300°C and the boiling point of mercury. The chemical reaction is represented by the equations:



The comparison of the conditions of the reactions proceeding in the mercury vapour bed and in the lead melt bed reactors shows substantial difference. When using lead, lead oxide is formed only on the surface of the bubbles, while in the case

of the mercury reactor, oxidation proceeds in the vapour zone at the boiling point of mercury to yield a smoke of fine distribution. Thus, a possibility is created for the reaction to proceed in the vapour zone on the presumably monomolecular catalyst surface.

In the presence of minute quantities of oxygen, no precipitation of mercury oxide was observed, although mercury oxide molecules may associate, owing to poor admixture, with the organic compound. The same phenomenon is met when oxygen is used in excess. This causes a substantial decrease in the specific surface area, which, however, remains even in this case much larger than that of other solid catalysts.

In this process, mercury is boiled in an iron container and liquid mercury is returned through a reflux cooler to the boiling vessel. The organic substance, contacting the mercury vapours, is oxidized over the mercury oxide primarily formed.

It may be seen that the mercury vapour bed reactor represents a transition from homogenous to heterogenous catalytic processes. Besides its large specific surface area, the Hg/HgO catalyst has the great advantage that the reaction conditions may be varied within very wide limits and heat dissipation and temperature regulating problems, constituting always a difficult task in oxidation reactions, can be readily solved. But then, it is a well known fact that mercury vapour condensers find a wide application as heat dissipators, for example in the temperature control of nuclear reactors. Heat transfer by mercury, on account of its great practical importance, has been thoroughly studied also from its theoretical aspect. Thus, heat transfer and the control of exothermic chemical reactions with the help of mercury have been dealt with in detail.

In cases, where the presence of mercury does not interfere either with the reactants or the catalyst, mercury can be

used in a system with reflux condenser for the internal regulation of the reaction. Constant temperature provided by the boiling mercury, can be varied within wide limits by the variation of pressure.

The vapour pressure of mercury in atmospheres between 350 and 650°C

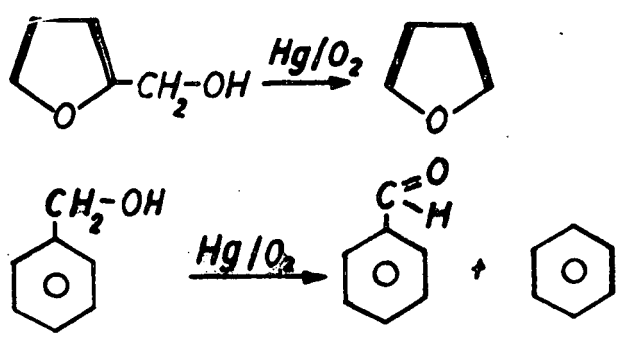
Temperature °C	Pressure atm	Temperature °C	Pressure atm
350	0,8847	530	11,27
380	1,497	560	15,41
410	2,408	590	20,60
440	3,733	620	26,97
470	5,567	650	34,68
500	8,035		

Further data, up to a temperature limit of 1300°C, may be calculated by the following equation:

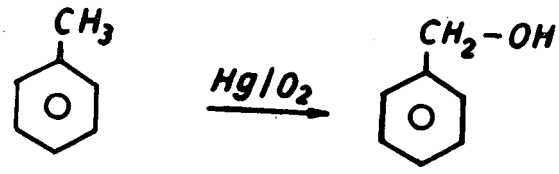
$$\log p = \frac{-52,23 \cdot 58,7}{T} + 7,75$$

The study of this possibility permitted the preparation of cyclohexene from cyclohexanol and ethylene from ethanol over an alumina catalyst. Thermal regulation was effected by boiling mercury, maintaining a temperature of 358°C.

With the help of the redox system Hg/HgO^{2+}, we succeeded in preparing furan from furfural, benzaldehyde and benzene from benzyl alcohol.



Besides these reactions, toluene could be oxidized to benzaldehyde in a yield of 20 per cent with a mercury oxide catalyst.



From these experiments the conclusion may be drawn that mercury oxide as catalyst is suitable for the realization of several oxidation reactions and in many cases can or may provide for specific properties and selective conditions different from those of other oxidizing agents. With the aim to obtain accurate knowledge on these possibilities, a detailed study of various organic oxidation reactions to be realized with a mercury-mercury oxide system in the reactor is advisable, as up to the present very scarce information is available in this field.

6. Description of the mercury vapour bed reactor

The mercury vapour bed reactor can be built from simple constructional elements. A description of the reactor /see Fig. 8/ is given in the following:

Mercury is boiled in an iron flask with external heating. The top of the flask is connected with an iron tube of 1 m length and 15 mm diameter, surrounded by an aluminium jacket with electric heating and regulation. Mercury vapours condense at the top of the iron tube and condensed mercury is returned through the side branch to the flask. In this design, contact time can be regulated independently of the feed rate of the reactants, because the rate of mercury circulation increases on increasing the heating rate of the flask, with a consequent decrease in contact time.

The compound participating in the reaction, for example furfural, flows from the feeding burette into the evaporator equipped with electric heating. Air is fed into the evaporator. To ensure a reproducible dosage, air is introduced into the evaporator through a multiple-stage reducing valve and a calibrated differential pressure gauge at a determined pressure. The mixture of furfural vapour and air enters over the mercury level into the reactor. The interior of the reactor is empty, or, if of great diameter, packed with Raschig-rings of various size. Furfural and air admix with the mercury vapour to form a homogenous gas mixture. Mercury is oxidized by atmospheric oxygen. The formed mercury oxide oxidizes furfural to furan carboxylic acid, which, in turn, is decarboxylized at the applied temperature.

The products are separated in a multistep condenser. In the first step, maintained at about 200°C, only mercury is condensed. In the following water cooled condenser, furan and other organic substances of high boiling point are separated. Next, furan is adsorbed by the active carbon column, connected to the top of the condenser. Only end gases and diluting gases, as for example N_2, CO_2, O_2, etc. pass through the gas meter. Furan is recovered from the carbon column by desorption with steam, under intensive cooling.

Liquids are fed from a burette into the reactor. Through a needle valve the individual substances can be fed uniformly into the reactor, provided the burettes are under an identical pressure of about 3 atm. Overpressure is established by connecting the burette with a pressure flask with an inert gas through a pressure reducing valve. Air may be supplied by the compressed air conduit, to which a pressure gauge is connected. The required volume of air, passing through a tap, a two-step valve and a buffer tank, is measured by a differential pressure gauge and is fed into the evaporator after control with a secured mercury manometer.

Besides the preparation of furan from furfural, also the oxidation of toluene to benzaldehyde and, on addition of Al_2O_3 catalyst, various dehydration reactions could be realized in the reactor. Measurements showed that the reactor gives optimum performance in the temperature range from 300 to 350°C and at an air feed twice the stoichiometric amount required for oxidation. Under these circumstances a conversion of 25 per cent could be attained.

The described mercury vapour bed reactor has a mercury vapour volume of 200 ml, and thus, a low specific capacity. For each reactor, intended also for industrial use, the dimensional scale-up procedure should be definitely investigated. With most types of reactor, scaling-up raises many new difficulties. The heat exchange of the heat of reaction evolved or absorbed during the reaction constitutes the greatest problem. In the case of the mercury vapour bed reactor, a ratio may be attained by varying the concentration of the air and of the organic compound, at which the amount of heat evolved during the reaction does not raise the temperature of the reaction mixture by more than 15°C. In this case, heat exchange with the walls of the reactor is of minor importance. Under these circumstances, the diameter of the reactor may be increased more or less arbitrarily.

Under consideration of this fact, a mercury reactor of 60 litre capacity, shown in Fig. 9, was constructed. The description of this reactor as well as the discussion of further details is contained in Volume VII.

7. Yellow and red lead oxide

Two modifications of lead oxide are known: the yellow modification /massicot/ and the reddish-yellow modification /litharge/. The transition point is 489°C. Below this temperature, litharge is the stable form, above this temperature

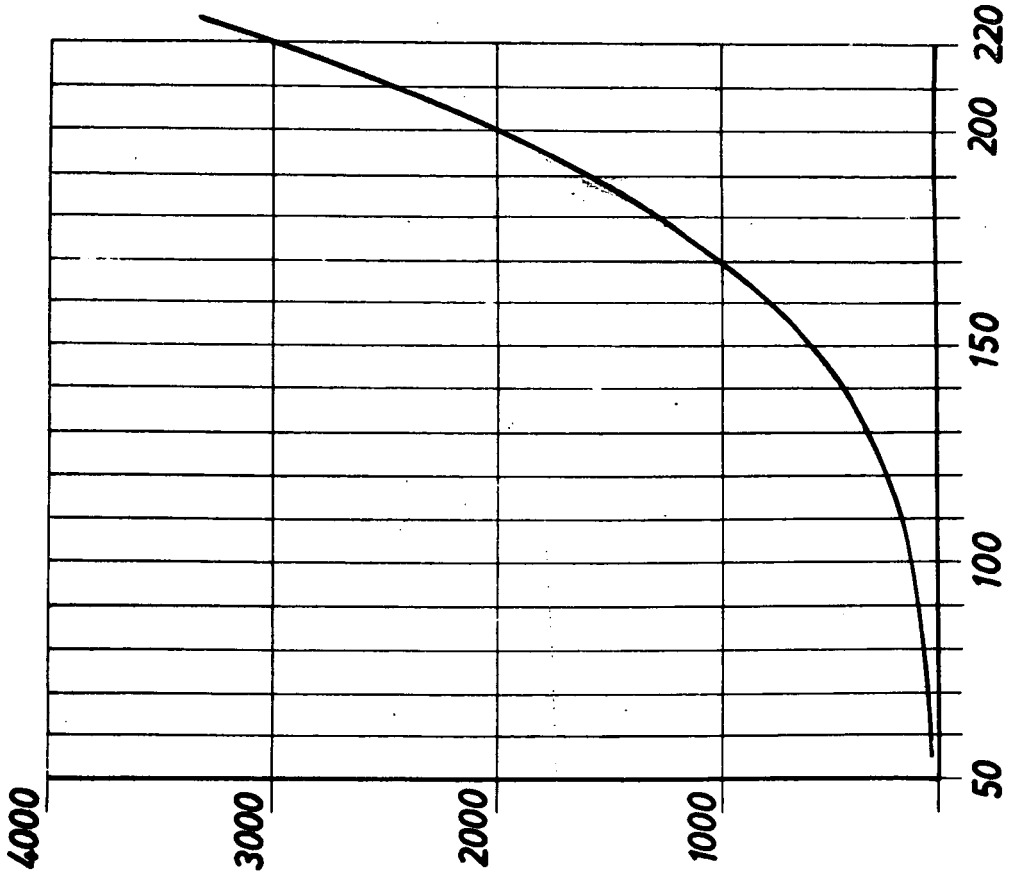


Figure 40
The vapour tension curve of furfural

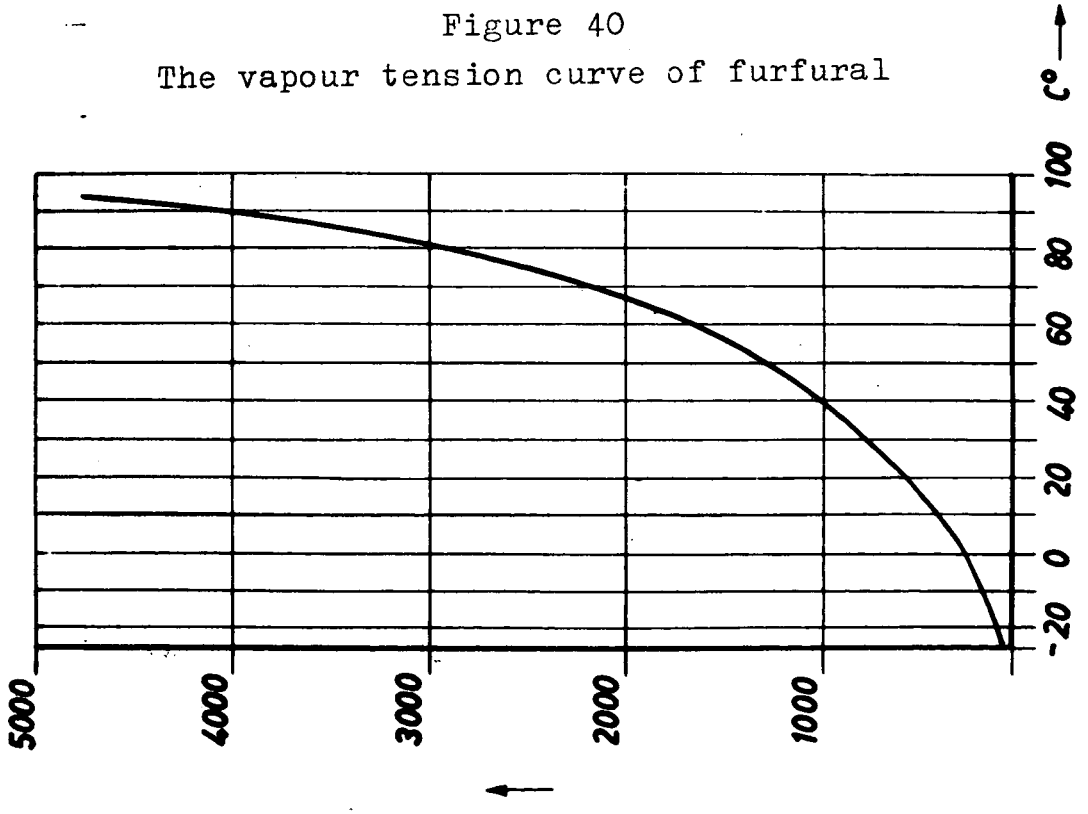


Figure 41
The vapour tension curve of furan

massicot. The two modifications differ in crystal structure, specific weight, solubility and reactivity.

	Cryst.form	Spec. weight	Solubility	Heat of formation	Heat of melting
Yellow lead oxide	rhombic	8,0	0,0023 g/ /100 ml of water at 22°C; alkali	-52,07	2,8 kcal $g\ mole^{-1}$
Reddish-yellow lead oxide	tetragonal	9,53	0,00175/100 ml water at 20°C; alkali, HNO_3, -52,83 lead acetate, NH_4Cl, $CaCl_2$	-52,83	0,4 kcal $g\ mole^{-1}$ /apparent/

In accordance with the difference in the heat content of the modifications, also their reactivities are different, but due to the slight difference, a substantial deviation is not to be expected. As mentioned already, above 489°C the yellow, below this temperature the red PbO is the stable form. Thus, keeping yellow PbO at a temperature below 489°C and red PbO above 489°C, respectively, the thermodynamically unstable form will convert into the other form. The rate of the conversion is a function of temperature.

E/ INVESTIGATION OF THE STRUCTURE OF CATALYSTS CONTAINING LEAD OXIDE CATALYST FORMULATIONS

1. Introduction

As evident on the basis of the theoretical part, the structure of the catalyst plays a very important role from the point of view of the efficiency of the catalytic oxidation of furfural to furan. From the theoretical aspect, the knowledge of the factors, determining the specific surface area of the catalyst - primarily the grain structure and the porosity - as well as of the factors determining the fine structure of the surface and its activity - thus primarily the crystalline composition - is necessary. Therefore, the above structural properties of preparations of possible practical use containing lead oxide have been investigated, both in their initial and reoxidized state. /This latter relates to the product obtained in the oxidation of pyrophorous lead formed in the process./ Investigations carried out up to the present, fall into three groups:

a/ Microscopic examination of the grain structure.
b/ Determination of porosity.
c/ Determination of the crystal structure and composition by X-ray diffraction analysis.

Experimental materials. Initial materials used most frequently in the tests were as follows: a/ technical lead oxide, b/ commercial minium, c/ ceramic-minium /a mixture of ceramic and minium/, d/ titanium dioxide - minium mixture.- The composition of the lead oxides will be given in detail in the reporting on X-ray analysis. Mixing proportion of the samples containing ceramics and titanium dioxide, respectively, was 60 per cent lead oxide or minium and 40 per cent filling material. Reoxidized samples were obtained by pyrophorous lead with air.

Experimental methods:Microscopic investigations were carried out with a "Microphot" camera microscope /Type D.15, Row-manufacture/. One division of the scale shown on the microphotos corresponds to 10 micron.

Porosity was calculated from measured data of specific /true/ and apparent density. Specific /true/ density was determined in a 1:1 mixture of ethanol: water, as preliminary wetting tests showed that this mixture is the best wetting agent of the oxides and mixtures to be tested. Apparent density /s'/ was determined in mercury according to literature.The pycrometric method was used for density determinations.

X-ray analyses were carried out with a diffractometer. /For detailed data see Paragraph c/ of "Experimental results"/.

2. Experimental results of the investigation of catalysts containing lead oxide

a/ Results of microscopic examinations /Figs. 42 and 43/

The microphotos of the initial and reoxidized samples are shown in Figures 42 and 43. Microphoto 42/1 shows technical lead oxide, 42/2 minium, 42/3 ceramic-minium, and 43/4 titanium dioxide-minium. Microphotos marked with a/ refer always to the initial, those marked with b/ to the reoxidized materials. Picture c/ of Figure 42/2 shows pyrophorous lead suspended in benzene.

Concerning microscopic granulation, the first three samples /lead oxide, minium,ceramic-minium/ show a distinct coarsening of the grain size. As a result of the catalytic process and following reoxidation, these materials formed lumpy aggregates of coarser granulation. In each case, the initial material was highly polydisperse.Many fine individual grains are to be observed among the greater grains. These fine

1/a
Initial technical lead oxide

1/b
Reoxidized technical lead oxide

2/a
Initial minium

2/b
Reoxidized minium

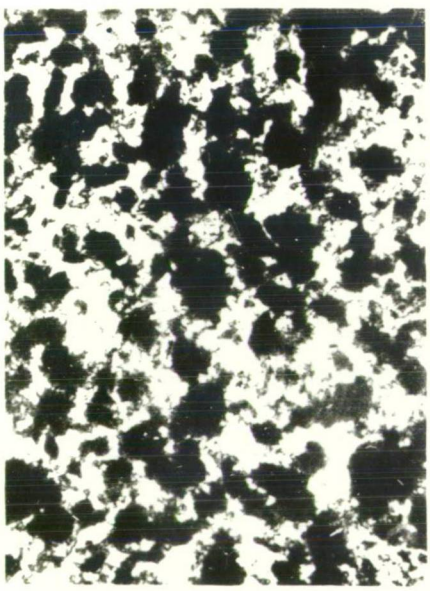
2/c
Pyrophorous lead

Figure 42

Microscopic examination of catalysts containing lead oxide

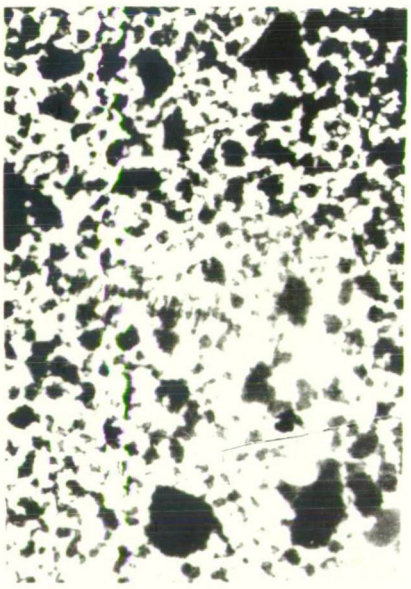
1/a.

1/b.



2/a.

2/b.



2/c.

3/a

Initial ceramic--minium mixture

3/b

Reoxidized ceramic--minium mixture

4/a

Initial titanium dioxide--minium mixture

4/b

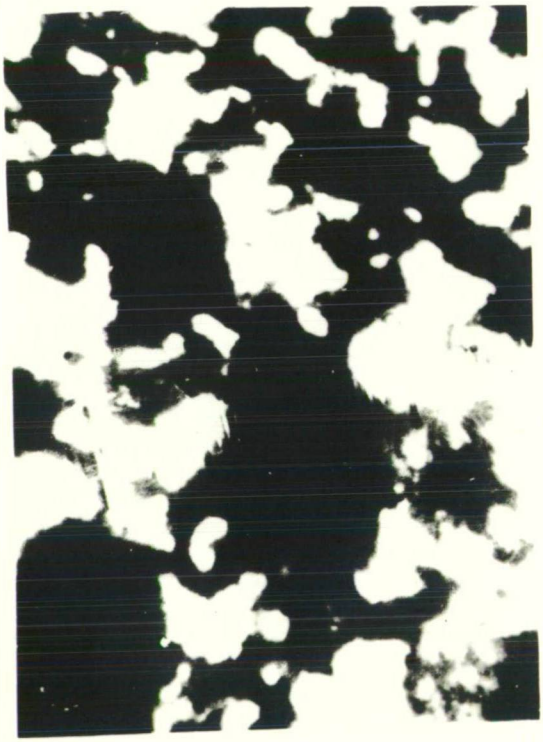
Reoxidized titanium dioxide--minium mixture

Figure 43

Microscopic examination of catalysts containing lead oxide

3/a.

3/b.



4/a.

4/b.

grains disappear almost completely in the reoxidized samples. This coarsening of the aggregation is the most pronounced with technical lead oxide, moderate with minium, and the lowest with minium containing ceramic material.

The titanium dioxide-minium mixture shows a different behaviour: Granulation, instead of coarsening, is even finer in the reoxidized sample, with the appearance of grains with characteristic, sharp contours. To these finding, the following qualitative observations may be added: whereas the coarsening of the first three substances during the process could be felt by the hand, reoxidized titanium oxide-minium mixture formed a powder of decidedly finer touch than the initial material. Also its colour changes: the initial mixture is pink, while the fine powder obtained after reoxidation is white.

Pyrophorous lead, which can be examined only as a suspension in benzene, has a very fine granulation and contains only a few coarse grains. Evidently, therefore, the coarsening of the aggregation does not occur during the catalytic process, but in the following reoxidation.

b/ Results of the porosity tests

Table 8 contains the specific and apparent densities of the initial and of the reoxidized substances.

Table 8

	s	s'	Porosity
Initial lead oxide	7,79	3,42	56,17
Reoxidized lead oxide	5,79	2,09	63,88
Initial minium	7,92	3,63	54,17
Reoxidized minium	8,22	3,22	60,83
Initial ceramic-minium	5,46	2,18	60,08
Reoxidized ceramic-minium	5,93	1,97	66,78
Initial titania-minium	3,70	1,76	52,43
Reoxidized titania-minium	3,77	2,00	46,96

It may be seen that true densities always increase slightly in the process[x/], while apparent densities generally decrease. An exception again is titanium dioxide–minium mixture. From true and apparent density values porosity /relative pore volume/ was calculated on the basis of the following considerations: Porosity is defined by the equation

$$\varepsilon = \frac{V_p}{V}$$

where V_p is the pore volume and V the total volume of the porous material, and thus:

$$V = V_r + V_p$$

where V_r is the true volume of the solid skelet. It follows from this that

$$\varepsilon = \frac{V - V_r}{V} = 1 - \frac{V_r}{V} .$$

If the true density of the skelet material /solid part/ of the porous material is s, the apparent density of the porous material is s' and the mass of the substance m

$$s = \frac{m}{V_r}, \qquad s' = \frac{m}{V}$$

and consequently

$$\varepsilon = 1 - \frac{s'}{s} = \frac{s - s'}{s}$$

and percentual porosity /per cent of pore volume/

$$V = \frac{s - s'}{s} . 100$$

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x/ Technical lead oxide appears to be an exception, this, however, is due to the fact that the initial material was contaminated with metallic lead and the absolute value of the initial density is therefore irreal.

Porosity values calculated in this way are shown in column 3 of Table 8. According to this, the porosity of lead oxide, minium, and ceramic-minium mixture increases and decreases only in the case of the titanium dioxide-minium mixture. The change, amounting to about 10 per cent, is not important.

c/ Results of X-ray investigations[x/]

Initial and reoxidized samples were finely ground and subjected to a detailed X-ray diffraction analysis. Generally samples gave sharp lines, the intensity of which, however, was different. This may be attributed partly to a difference in grain size, partly to preferential orientation. Figures 44-51 show the diffractograms of some of the samples, while the lines are listed in Table 9. On the basis of these data, five compounds: yellow PbO, red PbO, minium /Pb_3O_4/, anatase /TiO_2/, and lead titanate /$PbTiO_3$/ can be detected in substantial quantities in the eight investigated samples. $PbCO_3$, white lead /basic lead carbonate/, $PbSO_4$ and Bi_2O_3 occur in small quantities or in traces. Results pertinent to the individual samples may be summarized as follows:

Initial lead oxide /Fig. 44/ The spectrum lines of minium /Pb_3O_4/ are present, the three most intensive being 3.369 Å /100/:56; 2.898 Å /43/:21; 2.278 Å /43/:30, with the intensities indicated /in parantheses ASTM intensities are given/.

The lines of red lead oxide: 3.110 Å /100/:17; the second line /2.809 Å /62/ overlaps with the line 2.278 Å of Pb_3O_4, the third, 1.872 Å /37/:4, is significantly weaker. The lines of yellow lead oxide are very sharp: 3.067 Å /100/:51; 2.946 Å /31/:48 and 2.744 Å /28/:8.

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x/ István Náray-Szabó, Doctor of Chemical Sciences, Central Research Institute for Chemistry of the Hungarian Academy of Sciences.

On the basis of the diffractogram it may be stated that this preparation mainly consists of yellow lead oxide and minium, but contains also significant amounts of red lead oxide and traces of basic lead carbonate.

Reoxidized lead oxide /Fig. 45/. This sample contains but a small amount of minium; it consists chiefly of red lead oxide and of some yellow lead oxide. Traces of white lead /basic carbonate/ can be detected.

Initial lead oxide-titanium dioxide /Fig. 46/. Much red lead oxide, less yellow PbO and Pb_3O_4 appear from among lead oxides. TiO_2 is present in the form of anatase /rhombic/ in large quantities. $PbCO_3$, white lead, and traces of Bi_2O_3 are also present.

Reoxidized lead oxide titanium dioxide /Fig. 47/. In this preparation the lines of lead oxides have completely disappeared. Instead of them many of the $PbTiO_3$ lines appear at maximum intensities. Anatase is still present in lesser quantities. A few Bi_2O_3 lines of low intensity appear.

Initial minium /Fig. 48/. Pb_3O_4 lines are present with high intensity. The preparation contains also some yellow lead oxide and Bi_2O_3.

Reoxidized minium /Fig. 49/. The best part of the sample has transformed into yellow lead oxide. Very little Pb_3O_4 is present, $PbSO_4$ in trace quantities.

Initial ceramic minium /Fig. 50/. Besides the predominant Pb_3O_4 lines very little yellow PbO and Bi_2O_3 can be detected.

Reoxidized ceramic minium /Fig. 51/. In addition to predominant minium, fairly intensive lines of yellow PbO are present. Traces of Pb_2SiO_4 are indicated.

Figures 44 - 51

Figure 44: Initial lead oxide

Figure 45: Reoxidized lead oxide

Figure 46: Initial lead oxide + titanium dioxide

Figure 47: Reoxidized lead oxide + titanium dioxide

Figure 48: Initial minium

Figure 49: Reoxidized minium

Figure 50: Initial ceramic + lead oxide

Figure 51: Reoxidized ceramic + lead oxide

- 271 -

- 272 -

- 273 -

- 274 -

- 275 -

- 276 -

- 277 -

- 278 -

1. Initial PbO
2. Reoxidized PbO
3. Initial $PbO + TiO_2$
4. Reoxidized $Pb + TiO_2$
5. Minium
6. Reoxidized minium
7. Ceramic – minium
8. Reoxidized ceramic–minium

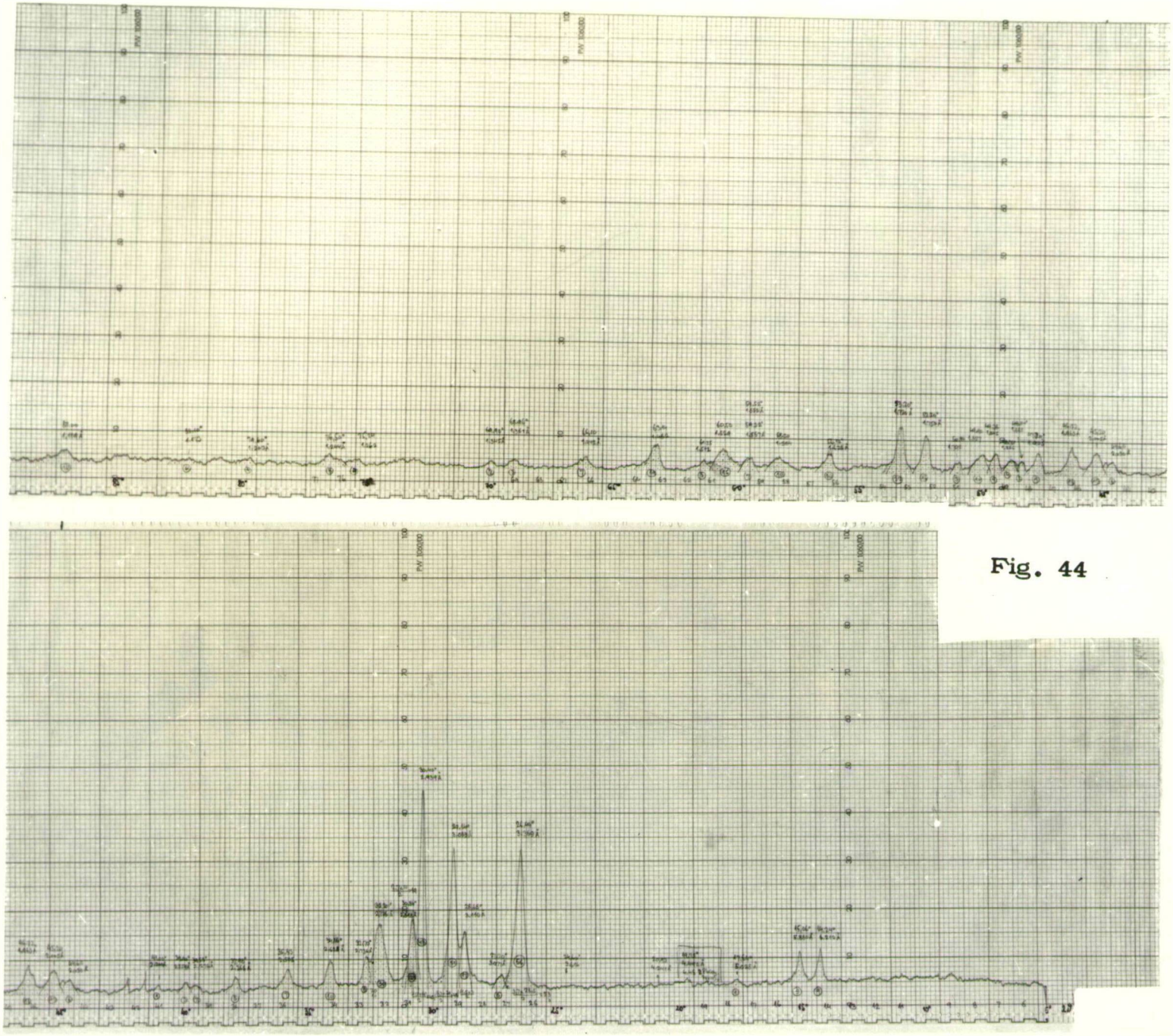
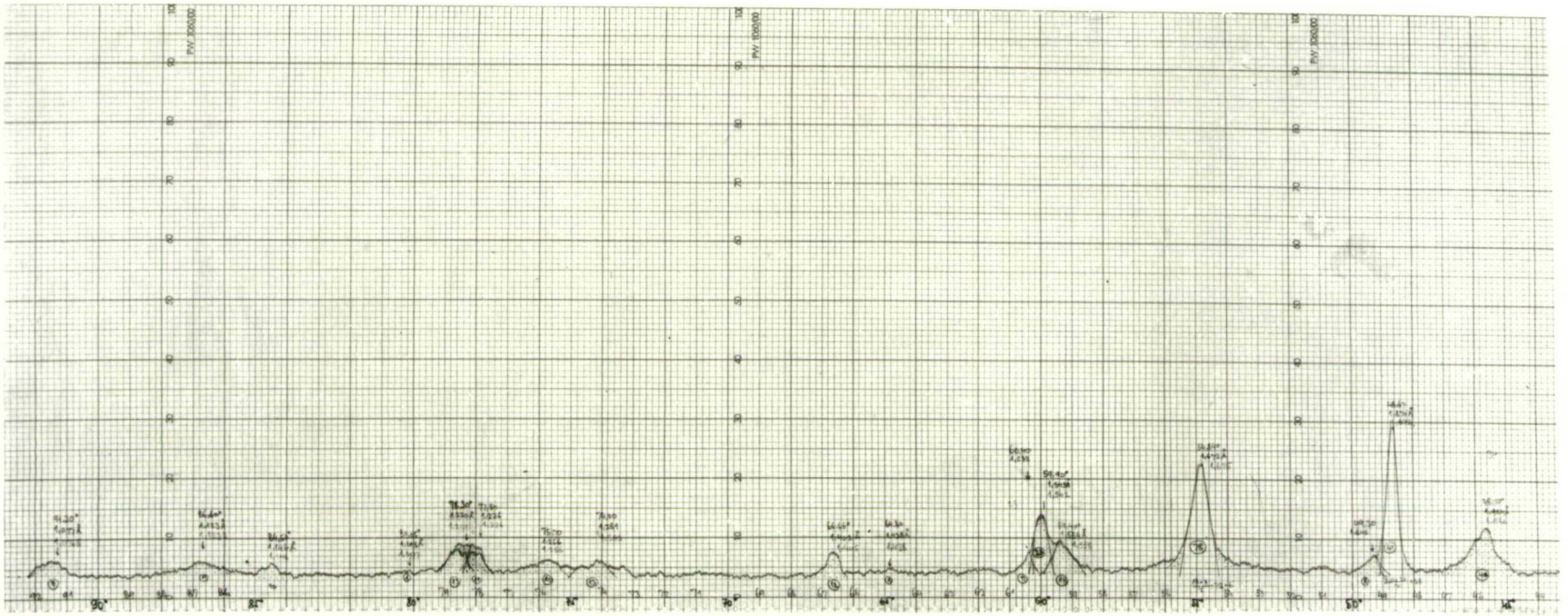


Fig. 44



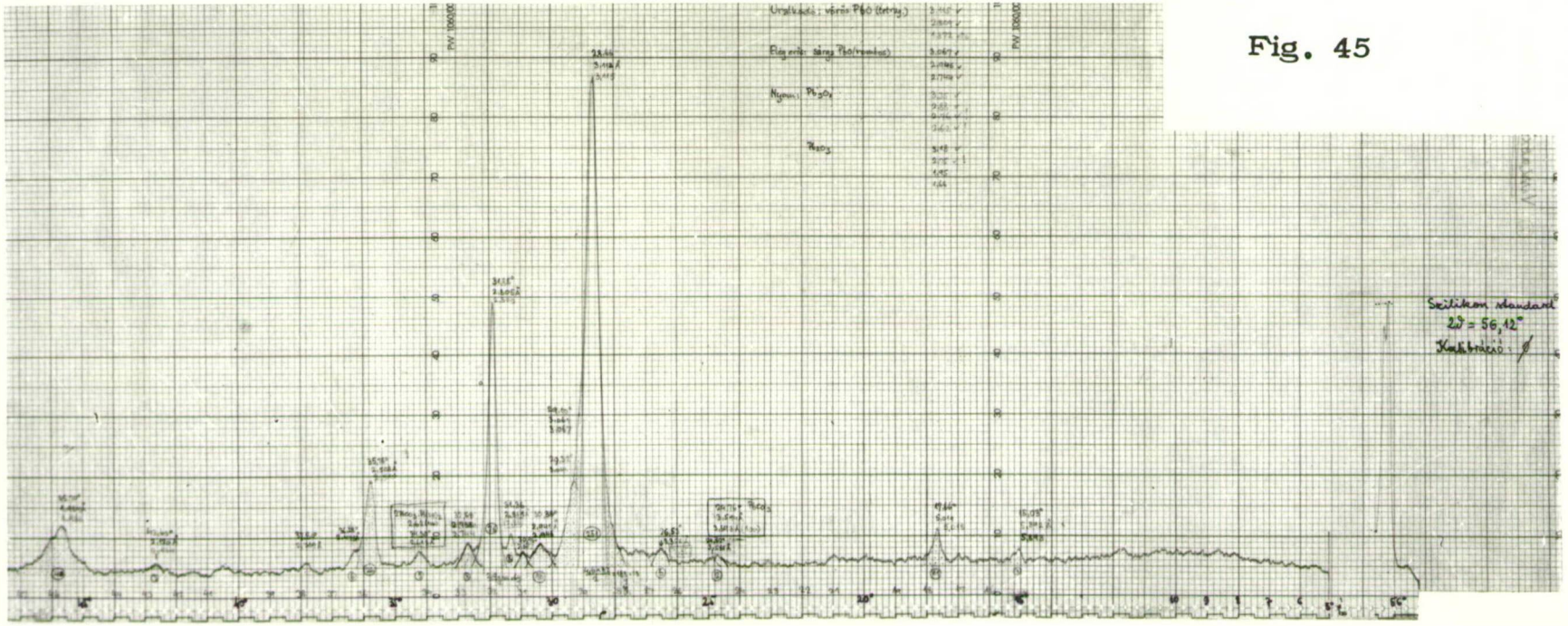


Fig. 45

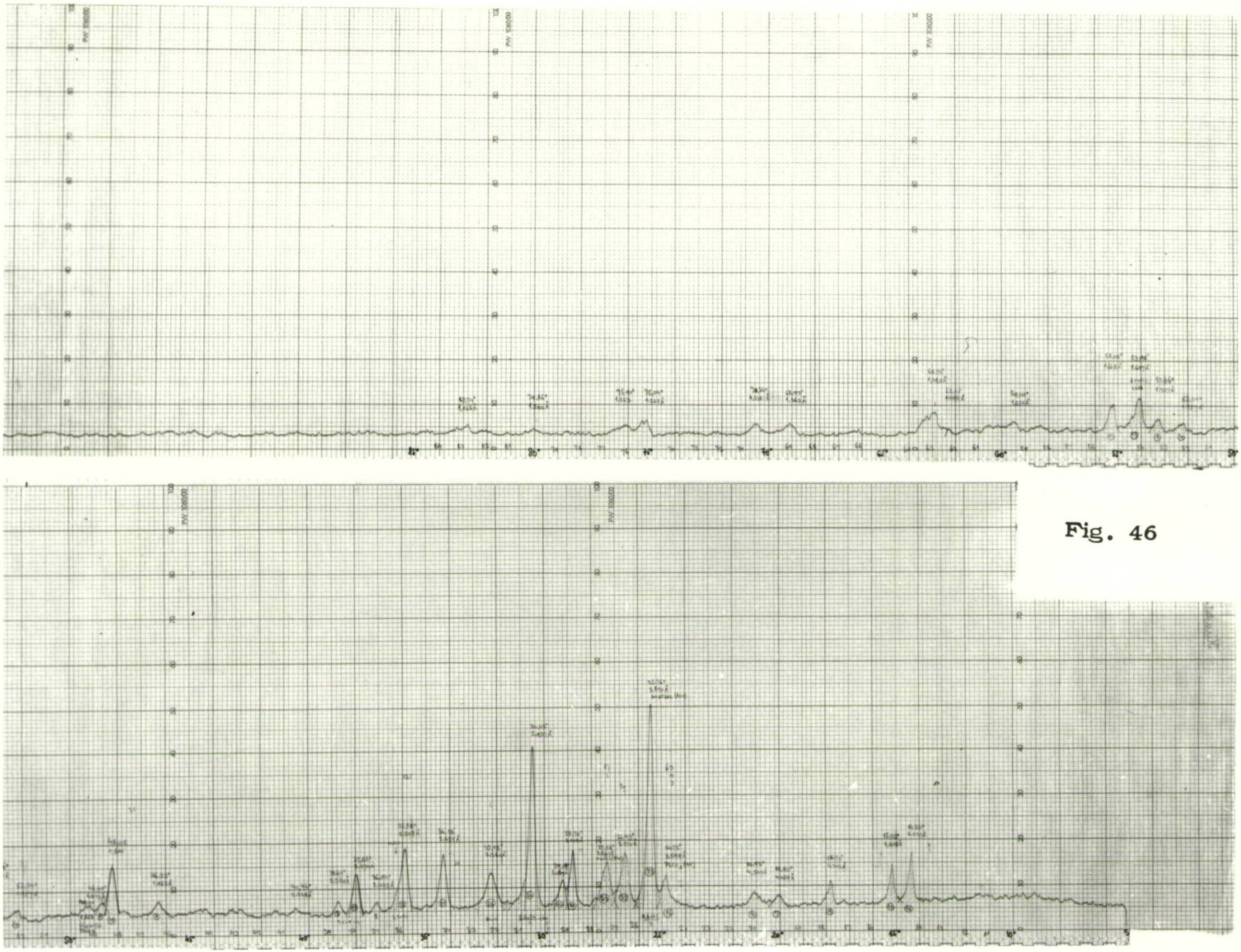


Fig. 46

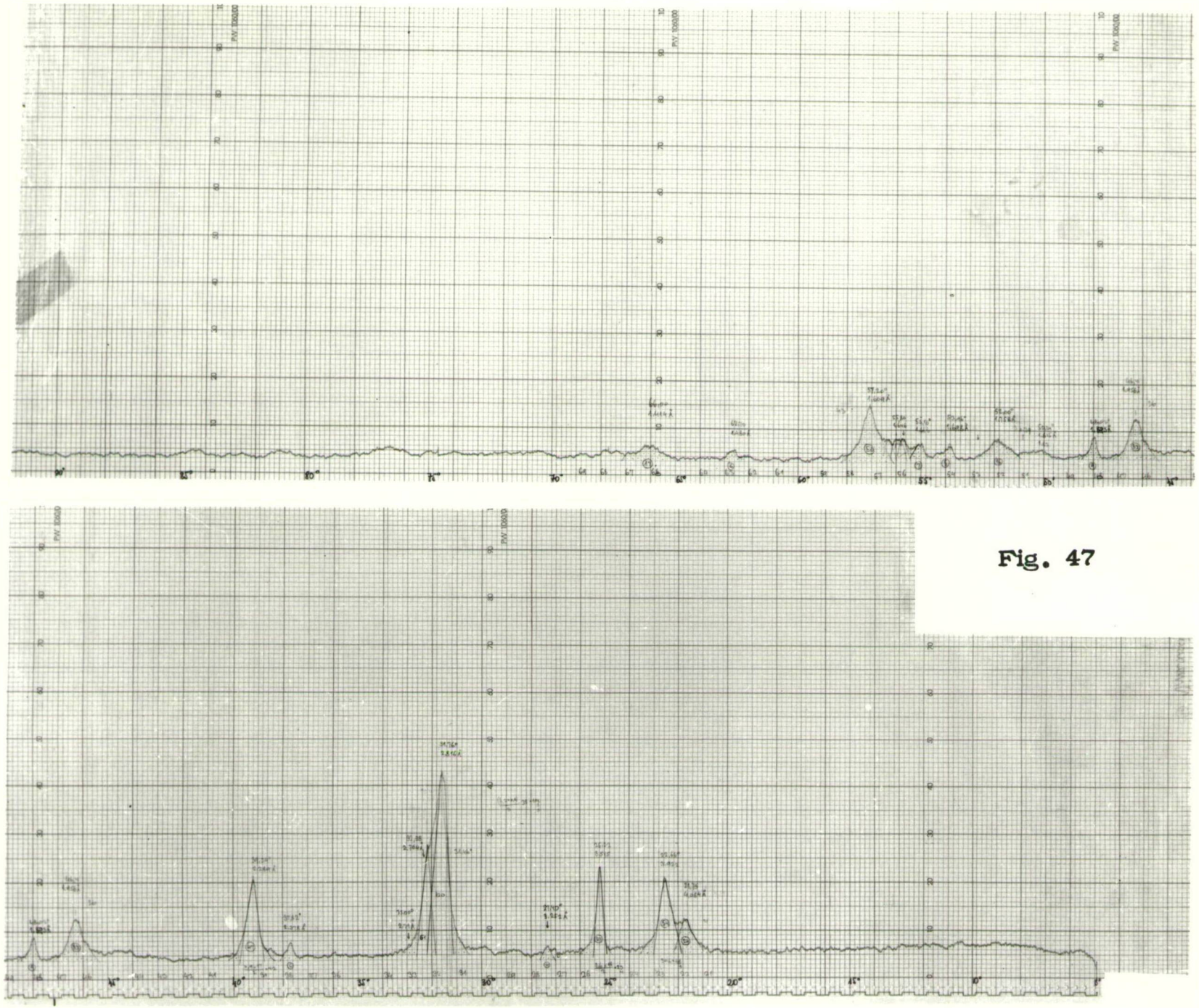


Fig. 47

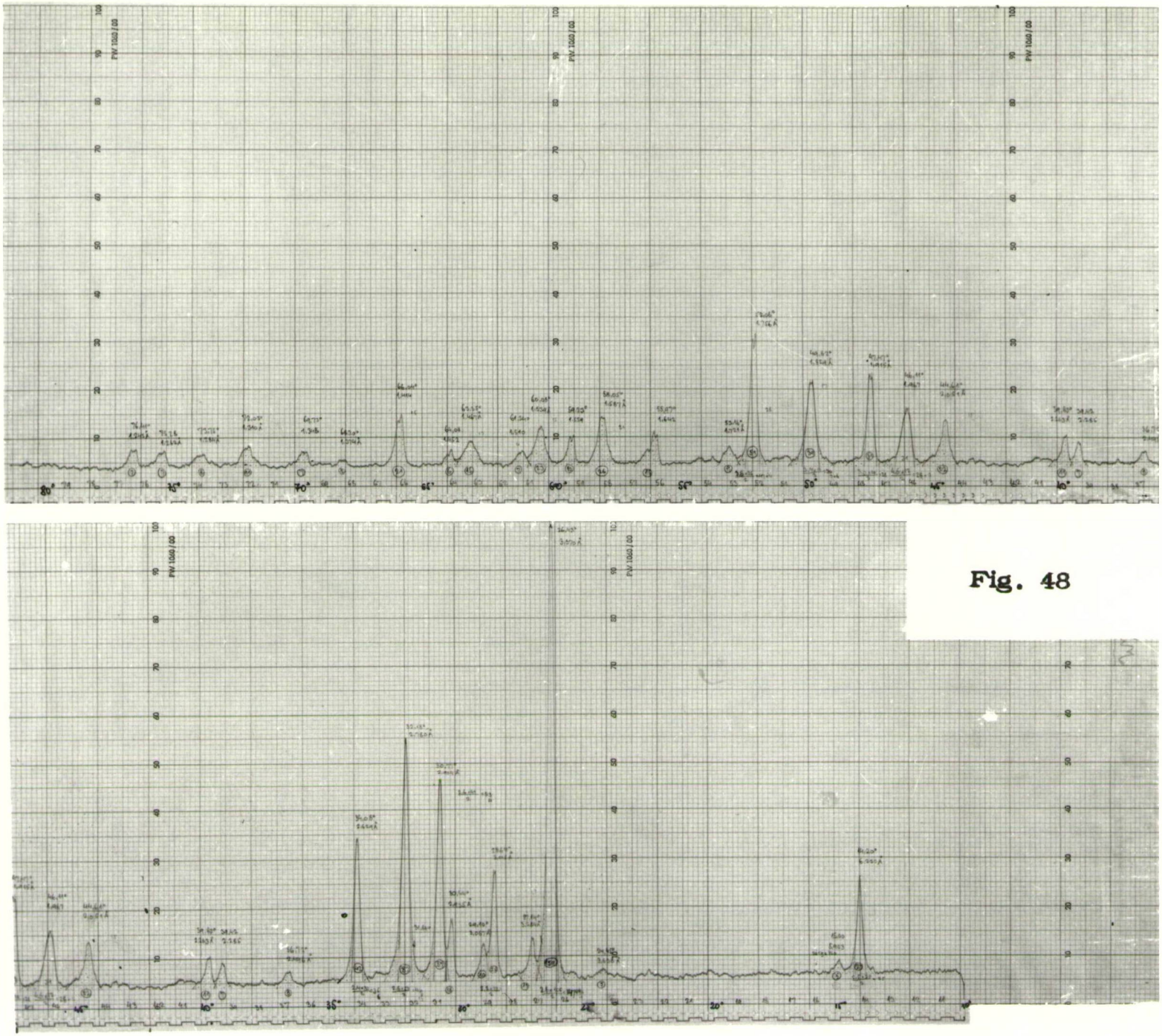
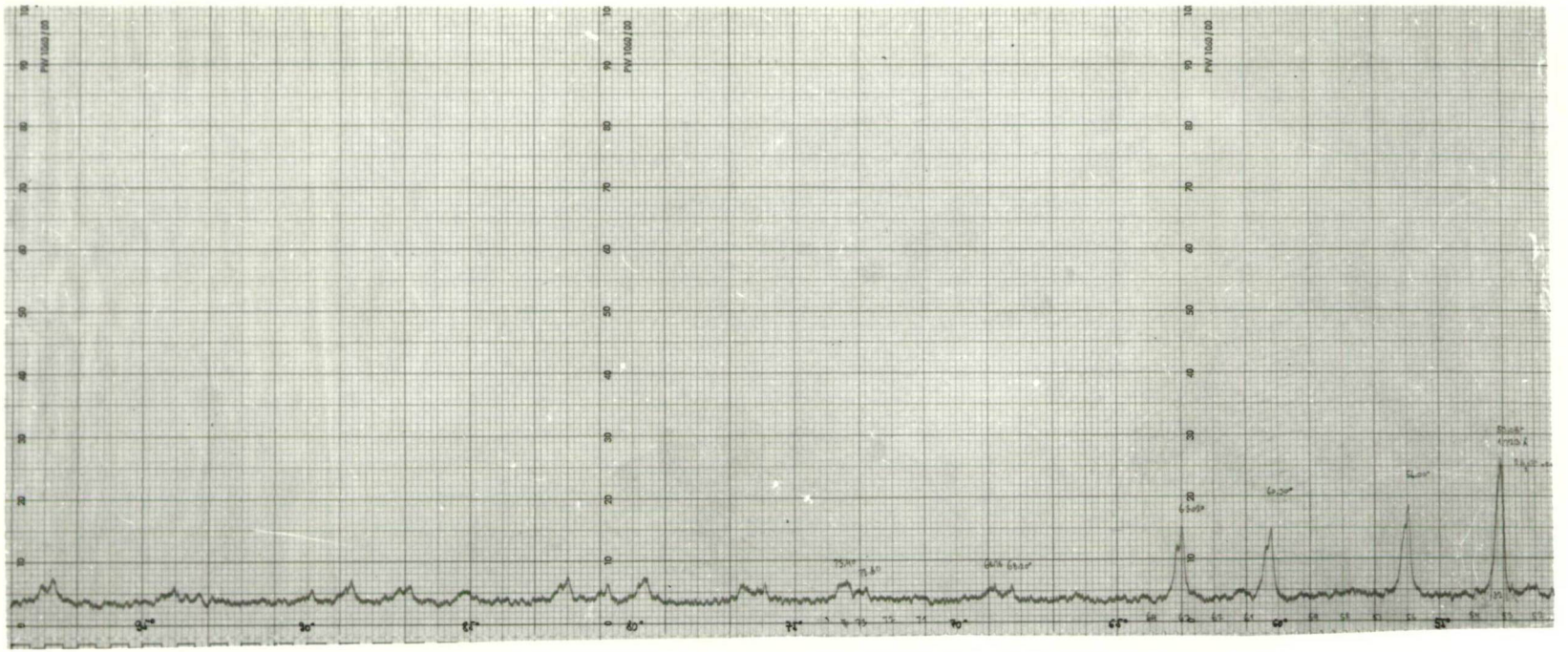


Fig. 48



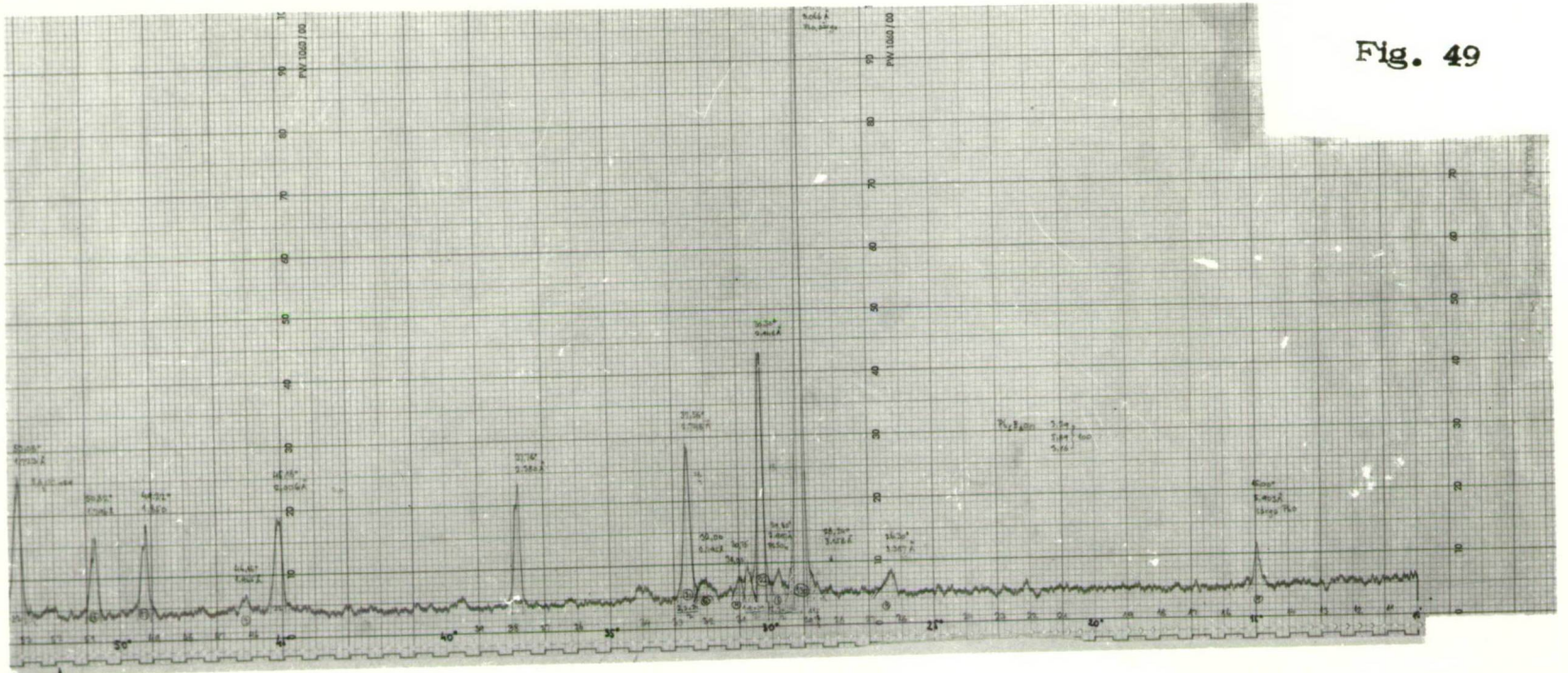


Fig. 49

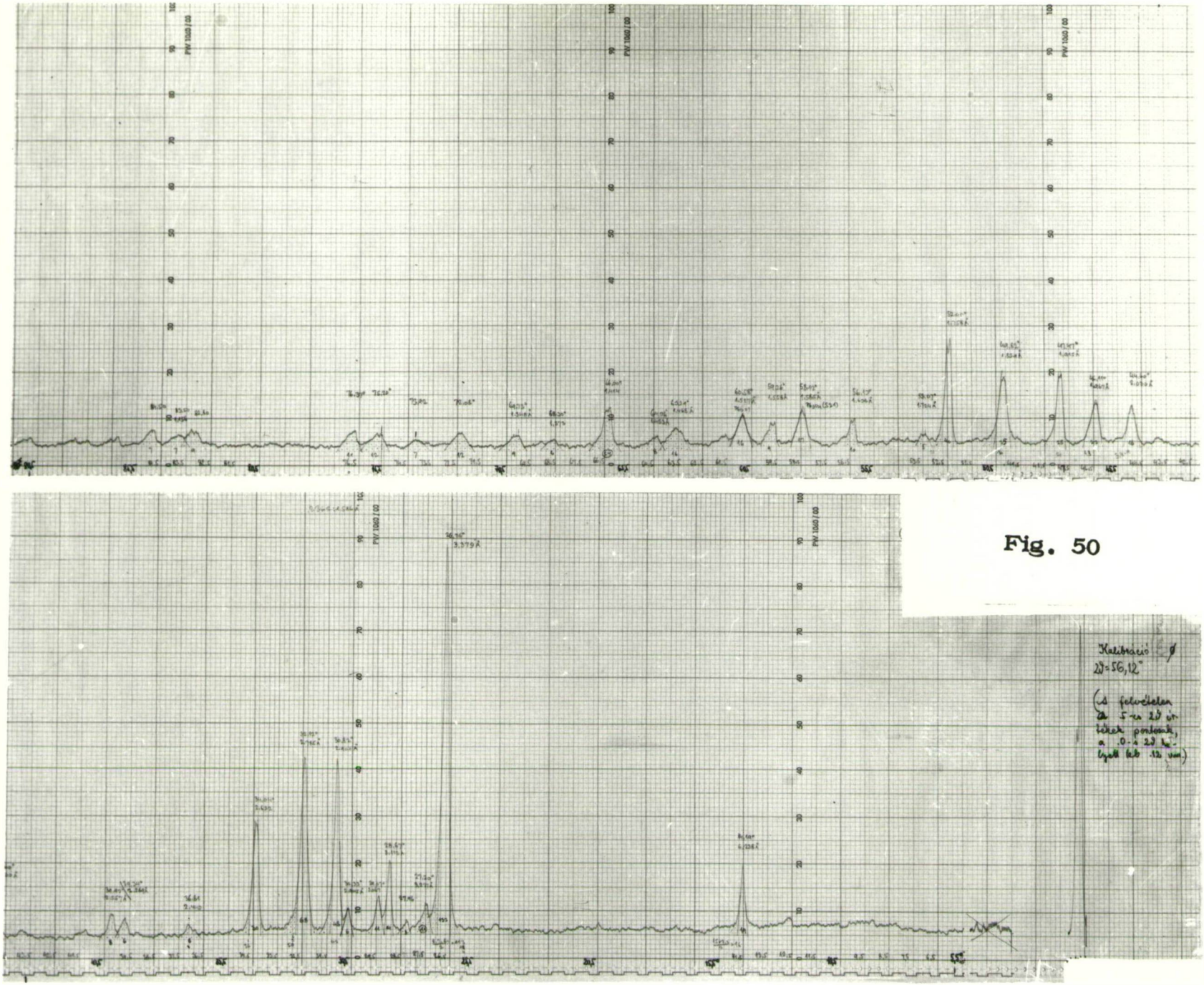


Fig. 50

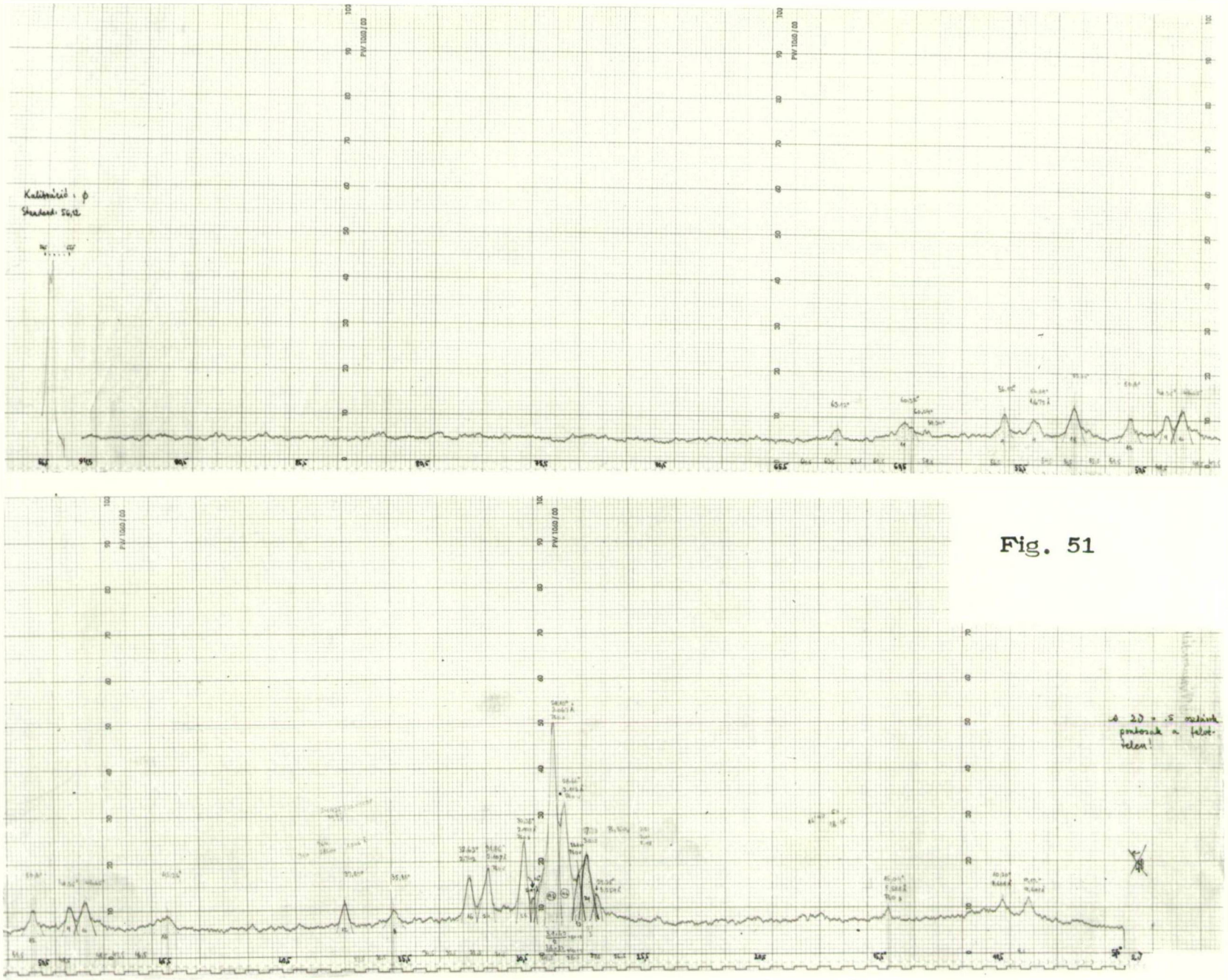

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Fig. 51

Table 9

Diffractometric examination of lead oxide and lead oxide-titanium dioxide catalysis

ASTM and literature					1. Initial PbO /Fig.44/		2. Reoxidized PbO /Fig. 45/	
2 v°	d Å	Int.	Compound	hkl	2 v°	Int.	2 v°	Int.
14.21	6.229	6	Pb_3O_4	110	14.24	9		
15.03	5.893	6	PbO_y	001	15.06	9	15.03	3
17.46	5.018	5	PbO_p	001	17.64	1	17.66	11
19.94	4.451	33	W.lead		19.75	1		
24.76	3.594	100	$PlCO_3$	111			24.76	2
26.36	3.379	100	Pb_3O_4	211	26.44	56	26.53	5
27.20	3.177	100	W.lead		27.20	5		
28.64	3.115	100	PbO_r	101	28.68	17	28.66	251
28.65	3.112		Pb_3O_4	220			Cannot be resolved	
29.10	3.067	100	PbO_y	111	29.14	51	29.10	
30.32	2.946	31	PbO_y	002	30.40	48	30.38	10
30.78	2.903	43	Pb_3O_4	112	30.84	21	30.96	3
31.46	2.842	100	$PbTiO_3$	101			31.36	8
31.84	2.809	62	PbO_r	110			31.88	75
32.16	2.782	43	Pb_3O_4	310	32.20	30		
32.60	2.744	28	PbO_y	200	32.70	8	32.68	8
34.04	2.632	28	Pb_3O_4	202	34.16	10	34.30	5
		100	W.lead					
35.76	2.510	18	PbO_r	002	35.83	7	35.78	26
36.10	2.438	32	$PvCO_3$	130			36.28	8
37.82	2.377	20	PbO_y	020	37.98	5	37.80	2
39.54	2.278	1	PbO_y	112	39.58	2		
40.40	2.23	25	W.lead		39.90	3		

Abbreviations: PbO_y = yellow PbO; PbO_r = red PbO; W.lead = white lead
Int. = intensity
d_o = lattice spacing
$TiO_z a$ = anatase
v^o = reflection angle /in degrees/

Intensities given here are relative intensities and only the lines of identical compounds can be compared quantitatively.

ASTM AND LITERATURE					1.Initial PbO /Fig.44/		2.Reoxidized PbO /Fig.45/	
2 v°	d Å	Int.	Com-pound	hkl	2 v°	Int.	2 v°	Int.
40.94	2.203	1	PbO_y	211	41.00	1		
42.52	2.124	1	PbO_r	102			42.62	3
44.60	2.030	17	W.lead		44.60	6		
45.12	2.008	12	PbO_y	202	45.20	13		
45.61	1.988	8	PbO_r	200			45.70	40
46.22	1.963	2	PbO_y	003	46.22	16		
					47.70	9		
48.22	1.886	28	Pb_3O_4	421	48.24	2		
48.60	1.872	37	PbO_r	112	48.76	4	48.67	41
49.24	1.850	14	PbO_y	212	49.38	9	49.30	8
49.84	1.829	28	Pb_3O_4	402	49.90	10		
50.78	1.797	14	PbO_y	220	50.94	2		
52.06	1.756	43	Pb_3O_4	332	52.20	15		
54.76	1.675	24	PbO_r	211			54.84	78
56.03	1.640	13	PbO_y	311	56.12	10		
58.10	1.586	14	Pb_3O_4	114	58.20	15		
59.28	1.558	6	PbO_r	202	49.32	7	59.40	18
59.95	1.542	11	PbO_r	103			59.40	23
60.30	1.534	9	PbO_y	222	60.50	15	60.40	7
61.18	1.514	2	PbO_y	213	61.25	5		
63.05	1.474	11	PbO_y	131	63.14	19		
64.80	1.438	2	PbO_r	113			64.80	1
66.10	1.412	14	Pb_3O_4	314	66.10	7		
66.50	1.405	5	PbO_r	220			66.66	12
68.85	1.363	1	PbO_y	114	68.96	3		
					69.90	2		

ASTM and literature				1. Initial PbO /Fig.44/			2. Reoxidized PbO /Fig.45/	
2 v°	d Å	Int.	Com-pound	hkl	2 v°	Int.	2 v°	Int.
73.90	1.282	2	PbO_r	301.203			74.00	13
75.65	1.256	3	PbO_r	310			75.70	10
76.50	1.244	2	PbO_y	402	76.50	8		
77.80	1.226	4	PbO_r	222			77.84	11
78.35	1.2.9	5	PbO_r	311.2.3			78.30	13
79.60	1.203	4	PbO_y	133	79.60	4		
82.00	1.174	4	PbO_y	331	82.10	4		
84.50	1.146	2	PbO_r	114			84.50	10
86.60	1.123	2	PbO_r	312	87.00	10	86.60	9
86.90	1.120	2	PbO_y	115	87.00	10		
91.30	1.077	3	PbO_r	312.223			91.30	8

3. Initial PbO + TiO_2 /Fig. 46/			ASTM			4. Reoxidized PbO+TiO_2 /Fig.47/		
2 v°	d Å	Int.	Com-pound	2 v°	Int.	2 v°	d Å	Int.
14.20	6.233	16	Pb_3O_4	14.24				
15.02	5.895	13	PbO_y	15.03	6			
18.70	4.742	9						
19.90	4.459	7	Wh.lead	19.94	33			
20.92	4.244	10	$PbTiO_3$	21.40	26	21.75	4.084	24
			$PbTiO_3$	22.80	49	22.66	3.922	54
24.72	3.599	16	$PbCO_3$	24.76	100			
25.36	31.510	73	TiO_2a	25.36	100	25.32	3.515	27
26.43	3.370	27	Pb_3O_4	26.36	100			
27.28	3.267	23	Wh.lead	27.20	100	27.40	3.252	4

3. Initial PbO + TiO_2 /Fig. 46/			ASTM			4. Reoxidized PbO+TiO_2 /Fig. 47/		
2 v°	d Å	Int.	Compound	2 v°	Int.	2 v°	d Å	Int.
28.70	3.108	19	PbO_r	28.64	100			
29.08	3.069	10	PbO_y	29.10	100			
30.42	2.937	54	PbO_y	30.32	31			
			$PbTiO_3$	31.46	100	31.76	2.816	120
32.18	2.780	26	Pb_3O_4	32.16	43			
			$PbTiO_3$	32.43	52	32.38	2.764	61
35.80	2.507	25	PbO_r	35.76	18			
36.94	2.432	2	TiO_2a	36.90	9			
37.88	2.374	15	PbO_y	37.83	20			
			TiO_2a	37.80	22	37.82	2.378	6
40.46	2.228	2	$PbTiO_3$	39.20	40	39.34	2.289	47
46.23	1.963	9	PbO_y	46.22	2	46.40	1.956	32
48.08	1.891	18	TiO_2a	48.08	33	48.02	1.895	9
48.60	1.872	4	PbO_r	48.60	37			
52.04	1.757	4	Pb_3O_4	52.06	43	52.00	1.758	16
53.66	1.707	5						
53.98	1.697	13	TiO_2a	53.93	21	52.96	1.698	5
55.02	1.668	11	TiO_2a	55.12	19	55.10	1.666	7
62.74	1.480		TiO_2a	62.70	13	57.20	1.609	50
							$PbTiO_3$	57.25
68.92	1.362		TiO_2a	68.65	5	62.50	1.480	6
						68.00	1.414	17
							$PbTiO_3$	65.70

5. Initial minium /Fig. 48/			ASTM and literature			6. Reoxidized minium /Fig. 49/		
2 v°	d Å	Int.	Compound	2 v°	Int.	2 v°	d Å	Int.
14.20	6.233	27	Pb_3O_4	14.24				
15.00	5.903	5	PbO_y	15.03	6	15.00	5.903	9

5. Initial minium /Fig. 48/			ASTM and literature			6. Reoxidized minium /Fig. 49/		
2 v°	d Å	Int.	Compound	2 v°	Int.	2 v°	d Å	Int.
24.45	3.638	5	Bi_2O_3	24.51	10			
26.43	3.370	159	Pb_3O_4	26.36	100	26.30	3.387	8
27.14	3.284	13	Bi_2O_3	27.34	100			
28.64	3.115	25	PbO_r	28.64	100			
29.10	3.067	10	PbO_y	29.10	100	29.11	3.066	130
			$PbSO_4$	29.76	100	29.80	2.997	5
30.44	2.935	18	PbO_y	30.32	31	30.30	2.948	22
30.77	2.904	57	Pb_3O_4	30.75	43	30.75	2.906	5
32.18	2.780	87	Pb_3O_4	32.16	43	31.90	2.892	4
			PbO_r	31.90	62	32.00	2.795	6
			PbO_y	32.60	28	32.56	2.748	31
34.08	2.621	42	Pb_3O_4	34.04	28	33.90	2.642	
						34.10	2.627	
36.72	2.446	8						
			PbO_y	37.82	20	37.78	2.380	20
39.42	2.285	7						
39.82	2.263	11	Pb_3O_4	39.87				
44.61	2.030	22	Pb_3O_4	44.60				
			PbO_y	45.12	12	45.18	2.006	22
46.11	1.967	31	Pb_3O_4	46.09	14	46.16	1.965	3
47.47	1.915	31						
			PbO_y	49.24	14	49.22	1.850	17
49.82	1.829	39	Pb_3O_4	49.85				
			PbO_y	50.78	14	50.82	1.796	15
52.08	1.756	51	Pb_3O_4	52.06	43			
53.16	1.721	9	Pb_3O_4	53.02		53.08	1.723	32
			PbO_y	53.06	15			
55.97	1.642	15	PbO_y	56.03	13	56.00	1.641	
58.05	1.587	26	Pb_3O_4	58.13	10			

5. Initial minium /Fig. 48/			ASTM and literature			6. Reoxidized minium /Fig. 49/		
2 v°	d Å	Int.	Compound	2 v°	Int.	2 v°	d Å	Int.
59.23	1.559	12	Pb_3O_4	59.15				
60.08	1.539	23	Pb_3O_4	60.08				
			PbO_y	60.30	9	60.30	1.534	
61.34	1.510	7	Pb_3O_4	61.20	14			
			PbO_y	63.05	11	63.02	1.474	
63.35	1.467	15	Pb_3O_4	63.33				
66.04	1.414	21	Pb_3O_4	66.00	14			
68.20	1.374	2	PbO_y	58.32	1	68.20	1.374	
69.73	1.348	7						
72.03	1.310	11						
73.75	1.284	8	Pb_3O_4	73.90				

7. Initial ceramic--minium /Fig. 50/			ASTM and literature			8. Reoxidized ceramic--minium /Fig. 51/		
2 v°	d Å	Int.	Compound	2 v°	Int.	2 v°	d Å	Int.
14.19	6.238	19	Pb_3O_4	14.24				
			PbO_y	15.03	6	15.04	5.888	3
26.36	3.379	133	Pb_3O_4	26.36	100			
			Ob_2SiO_4	27.77	100	27.73	3.215	29
27.20	3.277	11	Bi_2O_3	27.34	100	27.35	3.259	8
27.96	1.189	3	Bi_2O_3	27.95	50			
28.67	3.112	14	Pb_3O_4	28.43		28.66	3.112	46
29.07	3.070	11	PbO_y	29.10	100	29.10	3.067	92
30.33	2.945	6	PbO_y	30.32	31	30.38	3.067	26
			PbO_r	31.90	62	31.86	2.807	24
30.82	2.900	48	Pb_3O_4	30.75	43			
32.12	2.785	48	Pb_3O_4	32.16	43			
			PbO_y	32.60	28	32.63	2.742	16
34.04	2.632	30	Pb_3O_4	34.04	28			
			PbO_r	35.76	18	35.88	2.501	8

7. Initial ceramic-minium /Fig. 50/			ASTM and literature			8. Reoxidized ceramic-minium /Fig. 51/		
2 v°	d Å	Int.	Compound	2 v°	Int.	2 v°	d Å	Int.
36.8.	2.440	6						
			PbO_y	37.82	20	37.87	2.375	12
39.34	2.289	6						
39.92	2.257	8						
44.60	2.030	16	Pb_3O_4	44.60				
			PbO_r	45.12	12	45.26	2.002	16
			PbO_r	48.62	37	48.65	1.870	16
			PbO_y	49.27	14	49.35	1.846	9
46.11	1.967	22	Pb_3O_4	46.09	14			
47.47	1.915	25						
49.82	1.824	35	Pb_3O_4	49.85				
			PbO_y	50.78	14	50.81	1.796	12
52.00	1.758	40	Pb_3O_4	52.06	43			
53.07	1.724	3	PbO_y	53.06	15	53.20	1.720	18
			PbO_r	54.76		54.89	1.672	
56.13	1.638	10	PbO_y	56.03	13	56.12	1.638	9
58.12	1.585	17	Pb_3O_4	58.13	10			
59.26	1.558	9	Pb_3O_4	59.35				
			PbO_y	60.30	9	60.32	1.533	11
60.58	1.527	16	Pb_3O_4	60.55	14			
63.29	1.469	16	Pb_3O_4	63.33				
			PbO_y	53.05	11	63.12	1.472	4
66.00	1.414	24	Pb_3O_4	66.00	14			

3. Summary evaluation of experimental results

Already the results obtained up to the present in the examinations of lead oxide catalysts reveal a few significant relationships. Microscopically observed aggregation and porosity always change together, showing, however, an apparent inconsistency: when the microphoto reveals coarsening, porosity increases, and when the microphoto shows the grains to become finer, porosity decreases. As a rule the process results in coarsening of the microscopical dimensions and a simultaneous increase in porosity; this is the case with technical lead oxide, minium and ceramic-minium. These materials do not undergo any radical change, affecting chemical composition or crystal structure. Contrary to this, X-ray examinations of lead oxide - titanium dioxide mixtures show that the lead oxide lines disappear almost completely to be replaced by the lines of lead titanate. This indicates that besides a change in the microscopic and submicroscopic structure, also the chemical composition and consequently the crystal structure is changed decisively during the process. The decrease in porosity may be explained by the complete coalescence of lead oxide and titanium dioxide particles to form lead titanate, a very fine, dense, white powder. Probably this is brought about by the formation of pyrophorous lead as an intermediate product. Pyrophorous lead has a very high reactivity, and combines at a relatively low temperature, i.e. at the temperature of reoxidizing, at about 350°C with titanium dioxide present.

It may be stated in summary that initial lead oxides are reduced to pyrophorous lead of high dispersivity in the course of the process, and when air is blown through, lead oxides are formed again on blowing with air. The reoxidized samples, however, are not of the same composition and structure as the original materials. Minium is converted mainly into yellow lead oxide, while titanium dioxide-minium mixt-

ures give lead titanate. In accordance with these conversions, the porosity of technical lead oxide, minium, and ceramic-minium mixture increases, while that of the minium--titanium dioxide mixture decreases. An increase in porosity is always accompanied by a microscopical coarsening, a decrease in porosity by an increase in microscopical fineness.

4. Preparation of catalyst carriers

a/ Pumice. Crush pumice and sieve out the required grain size with a suitable sieve. Wash with HNO_3, then with distilled water until the wash liquid becomes free of electrolytes. Dry at 110°C.

b/ Aluminium grits. Stir melted aluminium until it cools. Aluminium grits in lumps of various sizes is formed. Crush this material and sieve out the required grain size. When the operation is carried out in N_2 or other inert-gas atmosphere, the quality of aluminium grits improves.

c/ Aluminium oxide. α. Dissolve 5 weight per cent aluminium nitrate in distilled water. Bubble ammonia gas through the solution until it becomes strongly alkaline. By repeated decanting wash this aluminium hydroxide until the wash water gives a negative test for NH_4^+ and NO_3^-, respectively. Otherwise residual NH_4NO_3 content may cause an explosion in the dryer or in the reactor.

β. Dissolve pieces of metallic aluminium in a 10 per cent alkali solution. Add the metal in excess. When the evolution of hydrogen has stopped, pass CO_2 through the system until it becomes saturated. The properties of the precipitated aluminium hydroxide greatly depend on the conditions of the precipitation. Aluminium hydroxide precipitated from an alkaline solution with CO_2 generally has a microcrystalline structure, whereas the product obtained with method α/is amorphous if precipitated from a cold solution.

d/ Silica gel. Acids /even carbonic acid/ precipitate silicic acid from sodium silicate solution. Silicic acid precipitate is a colourless gelatinous silica hydrogel. Silica hydrogel is dehydrated /e.g. in a dessiccator containing a dehydrating agent or by heating/. The last traces of water can be removed only at high temperature. The product obtained by dehydration is silica gel.

5. Fillers for catalysts

If the carrier or catalyst is prepared from a pulpy mass, it is often advantageous to admix solid powders as filters to dilute the catalyst or to improve its physical and chemical properties. For this purpose, pulverized carriers, ceramics and porcelain clay, kieselguhr, titanium dioxide, etc. have given good results.

In the preparation of catalysts pulpy substances cannot always be mixed in a machine so as to give a product which, after drying, is free of dust at operation temperature. In such cases the addition of a solid porous material is often advantageous. Too rapid drying or contaminations of the catalyst may result in pulverulence. Pulpy catalysts may be pelleted on a tabletting machine or spread in a layer and cut up, or passed through a sodium press or a mincer-like device with a rotary blade. Optimum water content will be adjusted as required by the selected method.

In case of pulpy materials, the loading of carriers with active chemicals can be carried out by mixing. Dry carriers may be impregnated with one of the reagents, which is then precipitated with the other. Solutions serving as catalysts may be spread also in drying drums under stirring on the carrier. The wide variety of chemicals, available carriers, and substance of promising promoter action offers a virtually infinite number of variants in catalyst research.

6. Formulations

a/ Mix 50 parts by weight of yellow lead oxide ground to a fine powder in a ball mill, with 25 parts by weight of titanium dioxide and an aluminium hydroxide pulp containing 25 parts by weight of solids in a kneading machine or in a braying mortar, then granulate. Keep this moist catalyst in a drying oven with a water bath at 100°C for five hours.

After this period, continue drying at 110°C for another five hours. Next, raise the temperature in two hours to 200°C, and in further two hours to 350°C. The catalyst is now ready for use. Chemicals of technical purity may be used.

b/ Formulation a/ is repeated with the modification that instead of technical lead oxide precipitated lead hydroxide is used. The other required components are added to this latter in a proportion to give a solids content as specified above.

c/ Process 50 parts by weight of lead oxide, 25 parts by weight of titanium dioxide and 25 parts by weight of fine aluminium metal filings as described for formulation a/ and dry for the same periods at the same temperatures. The application of this catalyst is the same as that according to formula a/. This catalyst has a better heat conductivity than the preceeding catalysts.

d/ - e/ - f/ Formulations a/, b/, c/ are repeated, but lead oxide is substituted by zinc oxide.

g/ - h/ - i/ Formulations a/, b/, c/ are repeated, but lead oxide is substituted by tin oxide.

j/ - k/ - l/ Formulations a/, b/, c/ are repeated, but lead oxide is substituted by bismuth oxide.

m/ - n/ - o/ Formulations a/, b/, c/ are repeated, but lead oxide is substituted by cadmium oxide.

p/ Formulations a/ to c/ are repeated, with the difference that 1 to 10 parts by weight of ammonium metavanadate is incorporated into the catalyst. In case of pulverulence the aluminium hydroxide content will be increased.

r/ Formulations a/ to o/ are repeated, with the difference that 1 to 30 parts by weight of metal chromate or a mixture of metal chromates is added to the catalyst.

s/ Preparation of V_2O_5 catalyst on a carrier of 1000 g aluminium grists. In an evaporating dish on a water bath knead 55 g of ammonium metavanadate to a paste with as much water as it can take up. Heat to 60 - 70°C, and, under intensive stirring, add to it in small portions 85 g of oxalic acid over a period of 15 minutes. This causes the liquefying of the substance and a change of its colour, to give finally a thick blue solution of high viscosity. Keep the solution under continuous stirring for another 15 minutes at 70°C. After cooling, add drop by drop 21 ml of concentrated NH_4OH to the substance, to obtain a solution of intensive blue colour. To this solution add 1000 g of Al grits, dry after impregnation, then heat in air at 400 - 500°C.This heat treatment causes the complex to decompose. Heating is continued for about 12 hours, until the smell of ammonia disappears. This ignition can be carried out also in the reactor. The upper temperature limit has to be strictly observed.

Chemicals can be applied quickly and uniformly in a rotary drum with infra-red drying on aluminium grits. V_2O_5 catalyst can be applied or formed in a more or less similar way also on the other carriers.

It should be mentioned here that the external parts of finished silica gel, when coming into contact with water or

aqueous solutions, become immediately saturated with water, swell and peel off of the dry internal core. To eliminate this disadvantage, silica gel is to be kept in saturated cold steam, and atmospheric humidity has to be slowly raised until a water vapour concentration corresponding to saturation at 100°C is attained. When equilibrium has been established, silica gel can be placed into an aqueous solution without incurring the danger of the mentioned phenomenon. Then, time is allowed for the impregnating chemical compound to attain equilibrium concentration in the aqueous solution and in the silica gel, respectively. After the establishing of equilibrium, silica gel is dried under slow stirring and under cautious raising of the temperature. The chemical compound used as catalyst will be most advantageously precipitated together with the carrier substance.

The procedure generally fails to result in a catalyst, which preserves under industrial conditions its physical properties, thus for example its strength. However, catalysts with permanent physical properties can be prepared according to the claims of patented processes, though patent specifications seldom disclose formulations. Vanadium pentoxide formed simultaneously with silica gel is an example for this very fact.

v/ Preparation of silver oxide catalyst. The catalyst is prepared from silver dust or from fine silver thread or net or lattice. Etching the surface with dilute nitric acid an advantageous surface layer can be obtained. Under stirring, filings may be etched also by electroplating. Filings can be pelleted. Pellets should not be cylindrical, because long cylinders hinder air flow. Lenticular granules proved suitable. On oxidation an oxide surface layer of not fully known structure is formed which has a catalytic action.

A silver oxide catalyst is obtained also by reacting silver nitrate with a stoichiometric quantity of alkali solution,

applied on a carrier, washed and dried. Naturally, both silver metal and silver oxide exert their catalytic action under oxidative conditions in form of the oxide.The preparation of silver oxide catalysts as well as that of vanadium pentoxide catalysts is the subject of a great number of patent specifications. These, however, are not easy to reproduce!

Silver metal of fine distribution is prepared generally by the thermic decomposition or by the reduction of silver compounds.

Note: The formation of furan from furfural under oxidative conditions is catalysed by almost every catalyst prepared for oxidation purposes.The following volumes contain further examples for the production of furan from furfural. In these volumes, as mentioned already in the theoretical part, this catalytic reaction serves as the model process of a special methodology and will be discussed in detail.

7. Summing up of some aspects of the research work on vapour phase catalytic processes

Our thoroughly discussed furfural-furan reaction served to make acquainted the user of the apparatus with research work in general on vapour phase heterogenous catalysis.The object of research work of this character is to determine experimentally the optimum conditions of the investigated reaction from the point of view of manufacture. Names of persons carrying out the work, the institute and the duration of the work must be reported. The volume of the reactor, the service life of the catalyst and its behaviour when work is interrupted, as well as the purity requirements and ageing properties of the catalyst must be given.The question must be answered whether the discussed reaction is considered suitable for industrial production, and the conditions requiring

further investigation must be pointed out. The reaction type intended for the next step in scaling-up has to be proposed. The evaluation factors of the reaction will be shown by diagrams, emphasizing optimum conditions. The composition of the catalyst will be described to facilitate reproduction.

The composition and purity of the reaction product shall also be given. The experimental task, the scope must also be clearly defined so that an answer may be furnished. The equipment and its operation, including starting up, operation proper, shutting down, and health and accident prevention requirements must be described. A typical reaction course must be enhanced. In reporting on the control of the reaction, analytical methods, their accuracy, and results of end-gas analysis shall also be given.

Experimental results must be summarized clearly. Concerning the controllability of the reaction, the most detailed information is required.

The loadability of the catalyst and its behaviour on a change in loading has to be investigated. The variation of conversion and yield in dependence on space velocity at different temperatures and at different initial gas concentrations are to be given. In case of a poor conversion, gravitational or mechanical recyclization has to be solved. The range of contamination, not yet harmful for the catalyst has to be determined. The service life of the catalyst becomes evident from the reproducible runs. The final report to be prepared on the termination of experimental work shall be complemented by drawings and tables.

Experiences pertinent to the positive or negative catalytic action of the reactor wall have to be reported, if possible, in dependence of time. Small observed details, characteristic of the reaction, must also be mentioned /evolution of smoke,

sweating or warming up of the adsorbent, etc./. In the summary evaluation, the possibility of the industrial application has always to be considered. Besides drawings, expediently also pictures of the developed equipment will be presented.

In the present volume, all these factors have been investigated and our model process was discussed with a view of these considerations.

-ooOoo-

Part IV

S U M M A R Y

S U M M A R Y

A complete series of vapour phase catalytic laboratories have been designed for industrial research institutes and for institutions of higher education. In these laboratories, the most various heterogenous catalytic processes may be carried out and studied. Our apparatus can be used for the experimental determination of the optimum reaction conditions of vapour phase catalytic processes already realized, for studies of scaling-up, for the investigation of catalysts, for research work on industrial and scientific problems, for educational purposes, etc.

The first unit of the planned and partly already realized twenty types of laboratories, with the accompanying book on chemical literature, laboratory practice and operators' manual, is designed for the preparation of furan from furfural by vapour phase heterogenous catalysis.

The first theoretical part of the book gives a comprehensive review on the structure and the most important reactions of furan and on the use of furan derivatives. Furan reactions of aromatic type, the use of furan derivatives in diene synthesis, reactions with ring cleavage, hydrogenation of furan and its derivatives, the synthesis of nitrogenous and other compounds starting from furan has been dealt with.

The scientific and patent literature on the production of furan were discussed in detail. A survey was given of the investigations carried out on the production of furan by the author and his coworkers in the University "József Attila" of Szeged. Reactors of a principally novel type: the melt bed, the mercury vapour bed, the disc, the plane-parallel etc. reactors, developed by us were described. A more thorough discussion of these reactors - with drawings of the apparatus, description of operation, detailed literature, etc. - will form the subject of subsequent volumes.

Part II deals with general knowledge pertinent to catalysis, thus, among others, with the influence of catalysts on activation energy, with the relation between the dispersity of the catalyst and its efficiency, with the action of activators, with the ageing and regeneration of catalysts, etc. The topics discussed include the adsorption of gases, the testing of adsorbents, and theoretical and practical knowledge on carbon-containing and on other adsorbents.

The preparation of pyrophorous metals, the heat content, the lattice characteristics and the dispersity of pyrophorous substances, the relation between pyrophorous properties and reactivity, as well as the use of pyrophorous metals as catalysts, with special consideration of the conversion furfural--furan have been discussed in this part.

Part III treats the production of furan with vapour phase heterogenous catalysis. General rules of work in a catalytic laboratory, handling of contact catalytic equipment, methods of feeding of the reactants, recovery of reaction products and their analysis are discussed in this experimental part. The apparatus evolved by us is described in detail. A report of a complete experimental run with an example of the necessary calculations, together with an example of the recording of experimental data is given.

Experiences gained with the earlier equipment are also discussed. The principal considerations in the planning of new experiments and the train of thought to be followed in the evaluation of the results are also mentioned. The most important factors in the development of new catalytic processes and in the investigation of catalysts, such as temperature, pressure, proportion of reactant, feed rate, composition and preparation of catalysts, selection of materials of construction for the reactor wall, possibilities of scaling up, determination of the maximum dimensions of the reactor, calcu-

lation of specific data characteristic of the proceeding of the reaction, economic and other aspects of the process are dealt with in detail.

In the description of the preparation of furan from furfural with metal oxide catalysts, the preparation of metal oxide catalysts and pertinent knowledge are exhaustively discussed. The redox system Hg/HgO and its use in the preparation of furan from furfural are covered, and an account is given of the mercury vapour bed reactor constructed by us for the realization of this process.

As an example for the testing of catalysts, methods used by us in testing the lead oxide catalysts, thus the microscopic determination of grain size, the determination of porosity, and the X-ray diffraction analysis of crystal structure and composition are reported in detail. Test data both of the initial and the used catalysts are given in tabular form, and the evaluation of the diagrams is discussed.

The preparation of catalyst carriers is covered. Several catalyst formulations are given. Considerations to be kept in mind in the thorough research into catalytic processes, which have been dealt with in the foregoing in detail are summed up.

The present volume, besides rendering account of several variants for the realization of the furfural-furan reaction and of the operation of several principally novel types of catalytic apparatus constructed by us for this purpose, makes us also acquainted with the general laws of vapour phase heterogenous catalytic processes. Further volumes will deal exhaustively with the special individual equipments, as for example the melt bed, the mercury vapour bed, the pyrophorous lead, the plane-parallel, the disc and other reactors, and cover further fields in this range of knowledge.

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Kiadványunk rövidítése

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I. kötet

DR. MÉSZÁROS LAJOS

Eljárás és készülék furfuralból történő furán előállítására gőzfázisú heterogén katalitikus módszerrel